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Systematics of the allotrope formation in elemental gallium films

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Abstract

Elemental gallium forms unusual allotropes, whose structures all differ distinctly from the close-packing of spheres typical for nearly all elemental metals. At standard pressure, four different crystalline allotropes are known where the \( \alpha \)-Ga allotrope is the thermodynamically stable one. Since the other allotropes can only be obtained under special conditions such as spatial confinement or undercooling, the structural relations among the gallium allotropes are not well-explored. We present here a systematic investigation of the dependence of the crystal structure formation in elemental gallium films on the deposition temperature and the subsequent annealing procedures using \textit{in situ} x-ray powder diffraction and Raman measurements, complemented by \textit{ab initio} calculations. The films were prepared with the femtosecond pulsed-laser-deposition technique on a substrate kept at constant temperature in the range of \(-190 \, ^\circ\text{C}\) to \(25 \, ^\circ\text{C}\), followed by cooling + heating cycles in the same temperature range. Besides preparing \( \alpha \)-, \( \beta \)-, \( \gamma \)- and amorphous Ga films as a single phase, a new gallium allotrope, \( \beta' \)-Ga, was synthesized, which is a distorted derivative of the \( \beta \)-Ga crystal structure. Furthermore, no direct transition between the \( \alpha \)-Ga phase on one side and the \( \beta \)-, \( \beta' \)-, and \( \gamma \)-Ga phases on the other side was observed in the solid state. Surprisingly, at room temperature amorphous gallium and below \(-60 \, ^\circ\text{C}\) the \( \alpha \)-Ga allotrope, respectively, is formed in the deposited films.

1. Introduction

In the periodic table of elements (PTE), which had originally been based on similarities of properties, the elements are ordered by atomic number, adding electrons one at a time. Fortuitously, many-electron effects mostly average out, and thus one can visualize the electrons successively filling the quantum states of the Coulomb potential in order of energy: with each new main quantum number, a new row (groups) represent the filling of the (orbital) angular momentum (and spin) quantum numbers. However, the PTE shows deviations from this ideal ordering in the sequence of occupied orbitals, such as the 3d-orbitals being ‘filled’ after the 4 s ones but before the 4p ones. This competition between shell 3 and shell 4 orbitals leads to a rift between groups 12 and 13 of the PTE. Since gallium is located next to this rift, the unusual properties of this metal are perhaps not too surprising: Bulk gallium is a brittle metal with a very low melting point (\( T_m = 29.8 \, ^\circ\text{C})\), shows a density anomaly upon solidification, is a diamagnetic solid, and the melt can be undercooled down to \(-180 \, ^\circ\text{C}\) [1, 2]. Furthermore, four structurally different allotropes of gallium are documented, whose structures are all uncommon for metals because they are not based on a close-packing of spheres [3]. The \( \alpha \)-Ga allotrope is the thermodynamically stable crystalline solid phase at ambient conditions and crystallizes in an orthorhombic lattice with 8 atoms per unit cell (\( Z = 8 \)) forming a layer structure containing Ga-Ga dimers [4]. The distorted honeycomb (100)-layers are stacked along the a-axis shifted by \( \frac{1}{2}2 \). The other three allotropes - \( \beta \)-Ga (monoclinic, \( Z = 4 \)) [5], \( \gamma \)-Ga (orthorhombic, \( Z = 40 \)) [6], \( \delta \)-Ga (trigonal, \( Z = 66 \)) [7] - are metastable and crystallize from the undercooled melt at \(-16.3 \, ^\circ\text{C}, -35.6 \, ^\circ\text{C}, \) and \(-19.4 \, ^\circ\text{C}\), respectively. The structure of \( \beta \)-Ga contains square-like arrangements of Ga-atoms forming layers parallel to (011), and the \( \gamma \)-Ga allotrope exhibits 5- and 7-membered rings in the (110) plane. The \( \delta \)-Ga structure
contains distorted icosahedra comparable to those observed in α-boron, another group 13 element. Figure 1 shows a schematic drawing of these crystal structures including selected crystallographic data (space group, temperature of formation, crystal density ρ, volume per atom V, atoms per unit cell Z, selected gallium distances d and the most notable structural feature (unit cells are highlighted by thin black lines). For α-Ga: the dimers are visualized by blue bonds, and one coordination polyhedron (1 + 6 neighbors) is shown.

A suitable method to investigate phase transitions of materials are thin film techniques, since the growth of a material can be controlled in a nearly ideal manner. In the past, both thermal evaporation and...
pulsed-laser-deposition (PLD) have been used to prepare films of elemental gallium. Deposition via thermal evaporation onto substrates near room temperature resulted in gallium nanoparticles with sizes ranging from 3 nm to 200 nm [21–24]. The optical properties of these liquid gallium particles have been studied, sometimes producing an ordering of the structures according to the optical excitations. Furthermore, the quench condensation technique has been used to obtain amorphous solid gallium films at −260 °C and β-Ga at −190 °C [25–27]. From the results as described, it is unclear whether the β-Ga allotrope exists between −260 °C and −190 °C. In addition, the pair correlation functions of amorphous and liquid gallium samples suggest atom arrangements similar to those in the β-Ga allotrope [28, 29]. In contrast, the laser ablation of elemental gallium has only rarely been employed. In one such case, the reflectivity of solid and molten gallium films, deposited onto silica substrates using an infrared laser, has been studied [30]. Furthermore, liquid gallium targets were used for the PLD of GaN films [31], and the ablation rates and thresholds of solid and liquid gallium targets were investigated using a nanosecond and a picosecond laser [32]. However, no specific structural characterization of the resulting films was performed. Similarly, ‘gallenene’, an atomically thin α-gallium layer obtained from solid-melt exfoliation, has been described [33], reminiscent of 2D (monolayer) materials such as graphene.

Summarizing the main results from the literature, we find that α-Ga has been produced at room temperature (bulk) and around −190 °C (film), whereas above room temperature molten Ga and below −260 °C the amorphous phase is formed, respectively. In the temperature range between 25 °C and −190 °C the metastable gallium allotropes were detected but only under special conditions such as spatial confinement or undercooling.

In this study, we present a systematic investigation of the allotrope formation in elemental gallium films deposited via femtosecond PLD at temperatures ranging from 25 °C to −190 °C. The phases generated by the deposition are studied in situ using x-ray powder diffraction and Raman scattering. In a second step, the deposits undergo heating + cooling cycles in the same temperature range mentioned above. The two methods involved, the deposition from the gas phase and the annealing of a material, are two completely different procedures for the generation of a (structured) solid, which can lead to different results: In the first approach, the solid is essentially built up in an atom-by-atom fashion, while the second one constitutes a rearrangement of the atoms inside an existing solid at a specific temperature. Their combination enables the analysis of structure formation of gallium at specific deposition temperatures followed by their phase transformations as function of the applied temperature schedule.

2. Materials and methods

2.1. Film preparation

The PLD experiments were run in an ultra-high vacuum chamber with a process pressure of 1 × 10⁻⁸ mbar for a period of 5–8 h per sample. As targets, pieces of a rod of gallium (99.9999%, MCP, Alperton, England) and tin (99.999%, Alfa Aesar, Heysham, Great Britain) ca. 10 mm long and 18 mm in diameter were mounted on a rotating target holder. The laser beam of a femtosecond laser (FemtoRegen, High-Q-Laser GmbH, Hohenems, Austria) with a wavelength of 516 nm at 442 fs was focused on target surfaces with a laser power of 20–30 mW (energy per pulse of 0.02–0.03 mJ at 1 kHz) and a spot size of 0.05 mm. The metals were deposited onto polished sapphire substrates (orientation 0001) and (1120), CrystTec GmbH, Germany) using a horizontal line scan of 50 mm s⁻¹ (HurryScan25 laser scanner, Scanlab AG, Puchheim; Samlight software, Scaps GmbH, Deisenhofen, Germany) where the targets rotated by 0.125 rpm. The ultra-short pulse laser minimizes the thermal diffusion length and accumulates the laser energy into a small volume of the target material. Thus, the solid gallium target does not melt during the ablation process despite of the low melting point near room temperature. The substrates (50 × 20 × 0.5 mm⁻³) were fixed on a copper sample holder which is connected to a transfer cart system to allow the positioning of the substrate 150 mm above the targets inside the preparation chamber (see figure 2(a)). The copper holder contains a resistance heater including a PT-100 thermal sensor and is connected to two pipes, which allow the cooling by a liquid nitrogen flow through the holder. During the deposition the substrate temperature was kept constant at 25 °C, 0 °C, −20 °C, −40 °C, −60 °C, −80 °C, −100 °C, and −190 °C via a temperature controller. Single crystal germanium (331) substrates and soda-lime glass (microscope slides) substrates were also used for gallium depositions at 25 °C and −190 °C, where no difference in the results compared to the sapphire, (0001) and (1120), substrates were observed. The residual gas was analyzed and monitored during the deposition process by quadrupole mass spectrometers (Prisma Plus QMG 220, Pfeiffer Vacuum GmbH, Germany). After the deposition the obtained samples (15 mm in diameter) were transferred directly, on the sample holder, from the deposition chamber to an x-ray diffractometer, while maintaining vacuum and cooling, by means of the special cart transfer system. The x-ray diffractometer is equipped with a Raman microscope for the in situ Raman measurements.
For the deposition of Ga on Sn, the three-region-method was applied (cf. figure 2(b)). In a first step, tin is deposited onto a sapphire substrate analogous to the gallium deposition described above, where the amount of Sn is similar to the amount of Ga used for the pure Ga deposition. Afterwards the substrate is laterally moved (by about 5 mm) in one direction, and then gallium is deposited. This results in three different adjacent sample regions: The one in the middle of the sample consists of gallium deposited on tin (notation: Ga\textsubscript{}/Sn\textsubscript{)}, while the two side areas consist of gallium and tin, respectively, that have been directly deposited on the sapphire substrate. This three-region procedure allows to compare in situ the properties of gallium films deposited on tin as well as on a sapphire substrate. In additional experiments, Ga and Sn were co-deposited on sapphire; here, the focus is on the influence of tin on the structure formation of gallium when the two elements are mixed on atomic level already at the deposition stage. The co-deposition of tin and gallium was performed by scanning the laser beam over the surface of tin and gallium targets in one move. Regarding the binary Sn-Ga alloy system, we recall that the Sn-Ga phase diagram shows that no intermetallic compounds are known in the solid state \[34]. A eutectic point exists at 13.7 wt% Sn and 20.6 °C, and a solid solution of gallium in solid \(\beta\)-Sn is observed up to a maximum of 4.3 wt% Ga at 21 °C \[35]. Furthermore, a metastable Sn\textsubscript{0.8}Ga\textsubscript{0.2} alloy that crystallizes in a primitive hexagonal unit cell has been obtained by rapid quenching \[36]. Thus, we expect that dissolution of gallium in tin can also take place in our deposited Sn-Ga films resulting in solid solutions.

2.2. Characterization

X-ray powder diffraction (XRD) patterns of the samples were measured in situ using a \(\theta/\theta\)-diffractometer (D8-Advance, Bruker AXS, Germany) with a Goebel mirror (Cu-K\(\alpha\)) inside a vacuum chamber (1 \(\times\) 10\(^{-7}\) mbar) in reflection mode. The chamber is supplied with a slit to absorb scattered radiation which considerably reduces the background under vacuum condition from 20° on in 2\(\theta\). Each x-ray pattern was monitored at an angle of incidence of 10° using an area sensitive detector (GADDS, Bruker AXS). During the in situ characterization cooling + heating cycles were successively performed: after the measurements of the samples as deposited, the samples were cooled down to \(\sim\)190 °C on the sample holder with a rate of around 2.5 °C min \(^{-1}\). Subsequently, the samples were heated up to 25 °C with a rate of around 0.5 °C min \(^{-1}\). This process happened stepwise where measurements were performed after each step. The lattice constants were refined by the Rietveld method using crystal structure data from the literature via the TOPAS software (TOPAS Vers. 4.2, Brucker AXS) with phase contents in percent weight (wt\%) \[37].

For the visualization of the crystal structures the software package Diamond version 4.4.1 (Crystal Impact GbR, Bonn, Germany) was employed using the cited crystal data.
In situ Raman spectra of the deposited films were recorded on a laser-microscope Raman spectrometer (iHR 550 spectrometer; BXFM microscope, manufactured by HORIBA, Bensheim, Germany) with confocal geometry attached to the diffractometer. The incident laser beam (532 nm at 10 mW) passes through a window into a vacuum chamber and is focused by an objective (100×) on the samples. The three-grating spectrometer is equipped with an internal filter wheel and a Peltier-cooled CCD camera (Synapsee). The resolution of the spectrometer (grating 1800 L mm⁻¹) is 1 wavenumber (cm⁻¹). Spectra were taken in quasi-backscattering geometry.

Scanning electron microscopy (SEM) images were acquired with a field-emission microscope (Merlin, Zeiss GmbH, Oberkochen, Germany) using an accelerating voltage between 1.5 and 5 kV and an Everhart-Thornley detector (SE), In-Lens detector, as well as an energy selective backscattered detector (ESB) for the material contrast. The samples were transferred into the microscope under argon using an in-house built transfer chamber.

The high-resolution transmission electron microscope (HR-TEM) images were performed at 200 kV in a JEOL-ARM 200 FTEM (JEOL, Tokyo, Japan), equipped with a cold field-emission gun and a CETCOR image corrector (CEOS Co. Ltd). The samples were directly deposited on TEM Cu-grids covered by lacey carbon films and subsequently transferred into the microscope via a liquid-N₂ cooling holder (Gatan, USA).

The Sn/Ga contents of the samples were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES; Vista Pro, Varian, Darmstadt, Germany). The samples were completely dissolved in conc. HCl (150 °C, Berghof-method) for the ICP-OES measurements. The values in the text represent contents in percent weight on metal basis (wt%).

2.3. Theoretical calculations
For the local minimization of the structures of the allotropes and the subsequent computation of the equation of state (EOS) E(V) (the dependence of energy E upon the conventional unit cell volume V), we employed the DFT-based codes CASTEP [38] and VASP [39].

With the CASTEP code, different exchange-and-correlation functionals (LDA, PBE and PBESol) and the ultrasoft gallium pseudo-potential [40] were used for calculations of the corresponding equations of states E(V). In that case, a cutoff energy of 354 eV was assumed in the plane-wave basis set. During the self-consistent electronic minimization, the eigen-energy convergence accuracy limit was chosen to be 1 × 10⁻⁶ eV/atom and the tolerance for the electronic total energy convergence during optimization was 1.0 × 10⁻⁸ eV/atom. The corresponding maximum ionic force tolerance was 3 × 10⁻² eV/Å, and the maximum stress component tolerance was 5 × 10⁻² GPa. Furthermore, the norm-conserving gallium pseudo-potential Ga_00.recpot of CASTEP (valence sub-shells are 3d, 4 s and 4p) and the cutoff energy for plane waves of 880 eV were used for calculations of Raman frequencies.

When using the VASP package [39, 41], the projector augmented-wave (PAW) method with a cutoff energy of 200 eV for the plane waves was employed [39, 41, 42] together with the corresponding pseudo-potentials. For the exchange and correlation terms, the gradient corrected Perdew–Burke–Ernzerhof (PBE) functional was used. The relaxation of the electronic degrees of freedom was controlled by the eigen-energy convergence tolerance of 1 × 10⁻⁶ eV/atom, and the maximum ionic force tolerance was chosen to be 2 × 10⁻² eV/Å.

The same calculation tasks have been performed using these two codes (CASTEP and VASP), different pseudo-potentials and exchange-and-correlation functionals (LDA, PBE, PBESOL) to obtain more reliable data for the tiny energy differences between structure allotropes of gallium. The dispersion interactions (vdW) were also taken into account when larger gallium supercells were used. This was done to check whether the energy relations between different gallium allotropes are largely insensitive to the vdW interactions.

For the comparison of different allotropic modifications of gallium containing different numbers of atoms in the unit cells, the equations of state E(V), calculated for the corresponding conventional unit cells, were presented scaled to one gallium atom, i.e. as energy/atom versus volume/atom curves.

Several results (mean squared displacement \( \delta^2(\mathbf{r}; T) \) as function of time and temperature, vibrational density of states \( G(\nu; T) \) as function of temperature, coordination number \( N_C(\mathbf{r}; T) \) as function of interatomic distance and temperature) for the gallium allotropes have been obtained from molecular dynamics (MD) simulations using the VASP code. The simulation time of these calculations was equal to 15 ps, with time steps of 1.5 fs using supercells of dimension 15 × 15 × 15 Å³, which contained about 500 atoms. For this purpose, the nMOLDYN tool has been utilized [43].

Finally, CASTEP was employed to compute Raman spectra of the different allotropes. The code uses a finite-difference method following the approach of Porezag and Pedersen [44]. In a first stage, one performs a full phonon calculation at the wave vector \( \mathbf{q} = 0 \) to determine the mode eigenvectors and identify the Raman active modes. Then CASTEP loops over the active modes only computing the Raman tensor, activity and depolarization for each [38]. Here, we have used the norm-conserving pseudo-potential for gallium (Ga_00).
recpot) supplied with the CASTEP code, because the Raman frequency calculations when using CASTEP may be performed only with this type of pseudo-potentials3.

3. Results

As described in the methods section, solid elemental gallium (99.9999%) was ablated under ultra-high vacuum by a femtosecond laser and subsequently deposited on single-crystalline sapphire substrates. During depositions the substrate temperature was kept constant at 25 °C, 0 °C, –20 °C, –40 °C, –60 °C, –80 °C, –100 °C, and –190 °C. In further experiments, gallium and tin were simultaneously deposited, and in another set of two-step deposition experiments, following deposition of tin films on a sapphire substrate, Ga was deposited using the three-region method (cf. figure 2(b)). Here the substrate temperature was kept constant at 25 °C and –190 °C. All these samples were structurally characterized as deposited by in situ x-ray diffraction and Raman measurements. Afterwards each sample underwent a sequence of cooling + heating cycles starting from the deposition temperature to study the stability ranges and possible phase transition of the gallium allotropes. The results from both the deposition and the subsequent thermal treatment procedures are summarized for the Ga and Ga-Sn experiments in the figures 3–5, and described in detail in the subsections 3.1–3.8; the results of the theoretical calculations are given in subsections 3.9 and 3.10. Note that the y-axis in figures 3–5 indicates the temperature at which the initial deposition stage of the process took place, while the x-axis represents the temperatures during the cooling + heating cycles. We have indicated the presence of all phases that are observed at a given stage of the cycle, using several colors in the figures. As criterion for the existence of a phase, we employed the powder diffraction and Raman data. We note that the XRD measurements that are performed at a discrete set of temperature steps require measurement times in the range of hours for each step. Since we only have a discrete set of temperatures where the measurements are performed, the value of the transition temperatures is only known up to the size of the temperature step, of course. This uncertainty in the value is indicated by a color gradient in the figures. Thus, the temperatures where the transitions between the different

3 For more details on the pseudo-potentials used for the various calculations, we refer to the supplementary information.
allotropes occur are identified by a significant signal of the corresponding allotrope detected by XRD/Raman measurements - the possible presence of nano-size particles that are not visible via XRD or Raman cannot be excluded, of course. Similarly, the finite time available for the experiment can result in situations where the transformation has not quite been completed in the sense that the new modification is still slightly distorted or some amount of minority phase is still present. We repeated the procedures and measurements for several different samples and observed the onset of the various transitions at the same temperatures in all samples; these temperatures are given in the text and in the figures.
3.1. Ga films deposited at 25 °C and 0 °C onto sapphire substrates

The deposition of elemental gallium at substrate temperatures of 25 °C and 0 °C on sapphire substrates forms light grey films. The topography of the Ga films was studied by scanning electron microscopy (SEM) and the corresponding images are presented in figure 6(a). The film consists of spherical droplets with diameters ranging from 5 nm up to 1 μm. The high-resolution images reveal that the deposit forms a very thin layer of gallium on the sapphire substrates on which the individual gallium droplets are located. Thus, the final gallium deposits at 25 °C and at 0 °C consist of isolated single droplets with a variety of sizes, and the substrate is not covered by a closed, dense gallium film.

After deposition in situ characterization by x-ray powder diffraction showed that the films are x-ray amorphous at room temperature. Subsequently the samples were cooled down to −190 °C via a liquid nitrogen flow through the sample holder, with a cooling rate of ca. 2.5 °C min⁻¹. At around −60 °C, the gallium films crystallized and this crystalline phase was stable down to −190 °C. Afterwards the flow of liquid nitrogen was stopped and the samples were heated up to room temperature (heating rate = 0.5 °C min⁻¹). During this process the gallium films transformed back to the amorphous state at around −20 °C (cf. figure SI-1 is available online at stacks.iop.org/MRX/6/116401/mmedia). A second cooling heating cycle - and also an intermediate annealing from 25 °C up to 40 °C (above the melting point), with a stay for about one hour at 40 °C, with subsequent cooling ≡, yielded the same observations. This structural evolution is shown at the top part of figure 3. On the left side the amorphous sample directly after the deposit is indicated by a grey area, and on the right side the subsequent cooling heating cycle with the crystalline Ga phase (indicated by a violet colour) is presented.

The set of reflections of the measured x-ray powder patterns at −190 °C does not coincide with any set that belongs to a known crystal structure of gallium (see figure 7). The greatest agreement is found with the β-Ga allotrope, but there are still several reflections left which do not exist in the β-Ga structure (e.g. around angles 36–37° and 58–60° in 2θ). Upon repeating the experiment five times, we observed nearly identical patterns for all samples deposited at 25 °C and 0 °C. Thus, we conclude that the origin of these observed x-ray patterns is an unknown allotrope of gallium which we call β-Ga because of the possible structural similarity to the β-Ga allotrope.

Starting the refinement from the monoclinic symmetry of the β-Ga structure with the space group C2/c (no. 15), all observed reflections can be accounted for in the subgroup P 21/c (no. 14) where the a-axis cell parameter of the unit cell of β-Ga is doubled. The structure refinement using these data, via the Rietveld method, is successful and the resulting crystal data are presented in table 1 (cf. figure SI-2 for Rietveld plot). In this context it should be mentioned that the measured x-ray powder patterns show intensity deviation (from the ideal random distribution of particle orientation) for some reflections caused by preferred orientation of the crystallites, a frequent issue in structure refinement based on film data. This texture effect had to be incorporated into the refinement procedure, complicating the determination of the crystal structure. Nevertheless, the gallium atom arrangement obtained in this refinement, as well as the atom-atom distances, are plausible, and ab initio
calculations of the E(V) curves of the different allotropes of gallium confirm the new $\beta'$-Ga structure as a reasonable solution (cf. subsection 3.9). Figure 8 shows the crystal structure of the $\beta'$-gallium allotrope. The $\beta'$-Ga crystal structure can be described as a derivative of the $\beta$-Ga structure: Both structures consist of rectangularly connected gallium atoms that form planar (011) layers in $\beta$-Ga (cf. figure 1) and twisted layers in $\beta'$-Ga, respectively.

Low temperature transmission electron microscopy (TEM) studies of these gallium films also support the existence of an, up to now, unknown crystalline gallium allotrope. Here, gallium was directly deposited on TEM grids, transferred into the microscope, and subsequently cooled down to $-175 \, ^\circ C$. The samples are amorphous at room temperature and crystallize during the cooling process. The d-spacing list obtained at $-175 \, ^\circ C$ contains some values that do not match any of the known gallium allotropes and furthermore are not compatible with

### Table 1. Crystal data and results of the Rietveld refinement of $\beta'$-Ga structure.

| Parameter                      | Value                      |
|--------------------------------|----------------------------|
| Temperature                    | $-190 \, ^\circ C$         |
| Cu-K$\alpha$ wave lengths, $\lambda$ [Å] | 1.54059, 1.54449          |
| measured angles (2$\theta$)     | 11.8–78.6 °               |
| crystal system                  | monoclinic                |
| space group                     | P2$_1$/c (no. 14)         |
| Z                               | 8                         |
| cell parameters [Å]             | $a = 5.200(1)$            |
|                                | $b = 8.446(2)$            |
|                                | $c = 3.314(1)$            |
|                                | $\beta = 87.11(2)$ °     |
| cell volume [Å$^3$]             | 145.35(5)                 |
| crystal density [g·cm$^{-3}$]   | 6.37                      |
| crystal size [nm]               | 110                       |
| number of reflections           | 87                        |
| preferred orientation           | spherical harmonics order 4 |
| Ga1 site                        | (4$c$)0.296(1), 0.123(2), 0.343(3) |
| Ga2 site                        | (4$c$)0.210(1), 0.632(2), 0.340(3) |
| $R_p$ [%]                       | 2.6(3)                    |
| $R_{wp}$ [%]                    | 7.0                       |
| $R_{Bragg}$ [%]                 | 9.9                       |
| $R_{Bragg}$ [%]                 | 2.2                       |
| distances [Å]                   | Ga–Ga: 2.62, 2.63, 2.71, 2.72, 2.74 |

$R_p$, $R_{wp}$, $R_{Bragg}$ and preferred orientation as defined in Topas Version 4.2 [37].
any unit cell as small as those of the \( \alpha \)-Ga and \( \beta \)-Ga allotropes. But the d-values can also be more or less consistent with the values of the \( \beta \)-Ga structure obtained from the powder diffraction data. The definitive assignment of the d-values obtained in high-resolution as well as in diffraction mode to one crystal structure was not possible. Note that the gallium particles were mobile under the electron beam.

In Raman measurements at room temperature on the gallium films deposited at 25 °C and 0 °C no Raman bands were observed in the amorphous phase. In contrast, the Raman spectra of these films measured in the \( \beta \)-Ga phase at −190 °C exhibit a broad slope increasing from 300 cm\(^{-1}\) to 100 cm\(^{-1}\), and it seems that one weakly discernible maximum occurs around 175 cm\(^{-1}\), where the calculated Raman spectrum for the \( \beta \)-Ga phase also exhibits several modes (cf. section 3.10). This general shape might be due to an overlap of several very broad peaks (see figure SI-3 - red curves -, and figure 16).

### 3.2. Ga films deposited at −20 °C and −40 °C on a sapphire substrate

Deposition in a temperature range from −20 °C to −40 °C results in light-grey Ga films, whose surface topography is analogous to the one of films deposited at 25 °C(cf. SEM images in figure 6(b)), i.e. spherical droplets with sizes in the range of 5 nm to 1 \( \mu \)m. The films are crystalline and show the powder pattern of the \( \gamma \)-Ga structure. Sometimes a small amount of a second phase identified as \( \beta \)-Ga (up to 15 wt%), is also visible in the x-ray powder patterns. Cooling the sample to −190 °C produced no changes in the x-ray patterns. The refined lattice constants match very well the constants of the \( \gamma \)-Ga structure [6] (cf. table 2). During subsequent heating to room temperature, the films transform to the amorphous state at around −20 °C, where first the \( \gamma \)-Ga fraction and then (if present) the \( \beta \)-Ga fraction converts. Surprisingly, during a second cooling these amorphous films transform into the new allotrope \( \beta \)-Ga at around −60 °C, which is then stable down to −190 °C. When heating the samples again to room temperature, they transform back to the amorphous state at −20 °C (see figure SI-4). Subsequent cooling + heating cycles deliver the same results as the second one. These structure evolutions are shown in figure 3 in the corresponding deposition temperature range. The \( \gamma \)-Ga and \( \beta \)-Ga phases are colored as cyan and brown in the deposit as well as during the cooling + heating procedure, and the transformation into the \( \beta \)-Ga phase during the second cooling cycle is indicated by the violet color.

![Schematic drawing of the crystal structure of the \( \beta \)-Ga allotrope. The gallium atoms are connected in a rectangular fashion, forming twisted (011) layers compared to the planar layers in the \( \beta \)-Ga structure (cf. figure 1); unit cell is highlighted by thin black lines.](Image)

**Figure 8.** Schematic drawing of the crystal structure of the \( \beta \)-Ga allotrope. The gallium atoms are connected in a rectangular fashion, forming twisted (011) layers compared to the planar layers in the \( \beta \)-Ga structure (cf. figure 1); unit cell is highlighted by thin black lines.

**Table 2.** Lattice parameters and crystal sizes of Ga films deposited on sapphire substrates at temperature \( T_{\text{deposit}} \) together with the corresponding literature values, for comparison.

| phase | \( T_{\text{measure}} \) | \( T_{\text{deposit}} \) | a | b | c | \( \beta \) | \( \rho_{\text{cryst}} \) | \( \lambda \) | References |
|-------|----------------|-----------------|---|---|---|--------|----------------|-----|----------|
| \( \alpha \)-Ga | 25 | −80 | 4.523(7) | 7.678(1) | 4.540(7) | 5.87 | 156 |
| \( \alpha \)-Ga | −190 | −80 | 4.497(6) | 7.661(1) | 4.531(7) | 5.93 | 66 |
| \( \alpha \)-Ga | −190 | −60 | 4.493(1) | 7.647(2) | 4.526(1) | 5.95 | 81 |
| \( \beta \)-Ga | −190 | −60 | 2.772(7) | 8.048(2) | 3.325(8) | 93.62(2) | 6.26 | 120 |
| \( \gamma \)-Ga | −190 | −20 | 10.590(2) | 13.597(3) | 5.111(1) | 6.29 | 56 |
| \( \alpha \)-Ga | 25 | | 4.523 | 7.661 | 4.524 | 5.91 | | |
| \( \beta \)-Ga | −25 | | 2.766 | 8.053 | 3.3332 | 92.03 | 6.24 | | |
| \( \gamma \)-Ga | −53 | | 10.593 | 13.523 | 5.203 | 6.21 | | | |
| \( \delta \)-Ga | −82 | | 9.087 | 9.087 | 17.02 | 120 | 6.28 | | |

\( T_{\text{measure}} \): Temperature at which the x-ray diffraction patterns were measured (in °C); \( T_{\text{deposit}} \): deposition temperature of the films (in °C); a, b, c, \( \beta \) lattice parameters (in Å); \( \rho_{\text{cryst}} \): crystal density derived from XRD (in g/cm\(^3\)); \( \lambda \): crystallite size derived from XRD (in nm).
Raman spectra of these samples show no (clear) peaks in the whole temperature range between 25 °C and −190 °C. At −190 °C the spectrum again exhibits a broad slope increasing from 300 cm⁻¹ to 100 cm⁻¹ (see figure SI-3 blue curves).

3.3. Ga films deposited at −60 °C on a sapphire substrate

The gallium deposition on sapphire substrates at −60 °C produces crystalline, light grey films consisting of isolated particles. The SEM images of these films presented in figure 6(c) disclose two different particle shapes. One class of particles are spherical droplets like those found after deposition at higher temperatures, and the other ones are more reminiscent of casting-like fragments of a frozen melt. Thus, the topology of these particles exhibiting two different shapes exist on the substrate, which are representative for the two different materials are in physical contact, which is not the case in these Ga −Ga, and β-Ga. The refined lattice constants correspond very well to the constants of the α-Ga [4] and β-Ga structures [5] (cf. table 2).

Upon heating to room temperature, the β-Ga phase transforms into the amorphous state at around −20 °C, while the thermodynamically stable α-Ga phase remains unchanged. At room temperature only the α-Ga allotrope is visible in the x-ray patterns. In a second cooling cycle, the amorphous phase transforms into the new β-Ga structure at around −60 °C, with no change in the α-Ga phase. No further changes in the x-ray powder patterns are observed down to −190 °C (see figure SI-5). A quantitative analysis of the powder pattern showed that the amount of the α-Ga phase was nearly the same as directly after deposition. From this, we conclude that the second cooling process - with the transformation from the amorphous state to the β-Ga allotrope is completely analogous to the behavior of the samples deposited at temperatures above −60 °C. Similarly, during a second heating stage, the β-Ga phase converts back to the amorphous state at −20 °C, alongside the unchanged α-Ga phase. As was the case for the samples deposited at higher temperatures, further cooling + heating cycles showed the same phase evolution as the second cycle. These cycles are again shown in figure 3 (at the deposition temperature), where α-Ga is represented by a green, β-Ga by a brown, and β-Ga by a purple color, respectively.

Thus, α-Ga is stable during the whole cooling + heating process, and its presence does not affect the phase transition of the rest of the material. At first sight, it might be puzzling that the crystalline α-Ga allotrope is unable to convert the remaining amorphous material into the stable allotrope as well by serving as a crystallization nucleus for the amorphous portion of the material. However, such a nucleation requires that both materials are in physical contact, which is not the case in these Ga films. According to the SEM images, separate particles exhibiting two different shapes exist on the substrate, which are representative for the two different crystal structures. By comparison with the results of the depositions above −60 °C, the spherical droplets can be identified as the amorphous phase or β-(or β)-Ga, and it follows that the casting-like fragments should correspond to the α-Ga phase. These physically separate parts of the deposit show different phase transformation behavior, and no transition between α-Ga on the one side and β-Ga, β-Ga or amorphous Ga on the other side, is observed in the experiments.

The Raman spectra of these samples measured at 25 °C exhibit the familiar broad slope starting at 300 cm⁻¹. However, at −190 °C bands between 150 cm⁻¹ and 250 cm⁻¹ are weakly visible. These bands can be assigned to the α-Ga allotrope, as can be seen by comparison with the Raman spectrum of α-Ga at low temperature discussed in subsection 3.4 (see figure SI-3, green curves).

3.4. Ga films deposited on a sapphire substrate at −80 °C, −100 °C, and −190 °C

The deposition of elemental gallium onto a sapphire substrate at temperatures of −80 °C, −100 °C, and −190 °C produces dark grey films. The SEM images (see figure 9) show rough, dense films, which cover the complete substrate, instead of the isolated droplets observed at higher deposition temperatures. The topography looks like a casting-like coating decorated with splashes of paint, where the darker color is due to the complete dense coating of the substrate. The films are crystalline and exhibit the α-Ga structure. This phase is stable during heating and cooling over the whole temperature range from −190 °C to 25 °C (see figure SI-6). The Rietveld refinements of the powder patterns reveal lattice constants which correspond - dependent on the temperature - very well to the constants of the α-Ga structure [4] (cf. table 2). The bottom part in figure 3 depicts the results of performing heating + cooling cycles after the deposition at low temperatures (green color indicates the α-Ga phase).

However, if the films are heated up to 40 °C (at a rate of ca. 1 °C min⁻¹), which is ten degrees above the melting point, followed by a very slow decrease to room temperature (ca. 5 °C/h) and subsequent cooling down to −190 °C (at a rate of ca. 1 °C min⁻¹), a completely different behavior with several phase transformations was observed. At the beginning, between 40 °C and −10 °C, the complete sample was x-ray amorphous. Upon lowering the temperature further, the x-ray patterns show the reflections typical of two crystalline phases: the
α-Ga and the β′-Ga allotropes. Considering the relative amounts of α- and β′-phases using Rietveld refinement, we find at −190 °C a ratio of around 15/85 wt%. During heating the sample up to 25 °C, we observed a transformation of the β′-Ga phase to the amorphous state at around −20 °C, analogous to the behavior found during the heating + cooling cycles of samples that had been deposited at higher temperatures. At room temperature, only the weak reflections due to the small amount of α-Ga are visible in the powder pattern (cf. figure SI-7). We conclude that for the crystallization from the melt, the formation of the β′-Ga allotrope is clearly preferred. We note that during this process the topography of the film changed as well. The SEM image in figure 9 (bottom) demonstrates that two kinds of particles exist after melting: casting-like fragments and droplets, which we can assign to α-Ga and amorphous gallium (or β′-Ga), respectively.

![Figure 9. SEM images (topography) of Ga films deposited at −190 °C on sapphire substrates. Top and middle images show two magnifications (note different scale bars); the bottom image was taken after the Ga film had been heated up to 40 °C after the deposition.](image-url)
The Raman spectra of the α-Ga films measured at 25 °C show only an unstructured ramp starting from 300 cm\(^{-1}\) to 100 cm\(^{-1}\), similar to those samples deposited at higher temperatures (above –80 °C). However, upon lowering the temperature, beginning around 0 °C, Raman bands emerge, and in the range from about –30 °C to –190 °C four sharp Raman bands at 250 cm\(^{-1}\), 220 cm\(^{-1}\), 193 cm\(^{-1}\) and 149 cm\(^{-1}\) are visible. Figure 10 presents the Raman spectra measured at 25 °C and at –190 °C in the range from 100 cm\(^{-1}\) to 500 cm\(^{-1}\). According to the six Raman frequencies we have calculated for α-Ga using the CASTEP program (cf. section 3.10) these bands can be assigned to the modes B2g\((2 \times)\), B3g, and Ag (see table SI-1). Furthermore, the measured Raman spectrum shows a strong increase at our lower measuring range limit at 100 cm\(^{-1}\), which is most likely associated with the two calculated mode frequencies at 89 \(1, 220\) cm\(^{-1}\) and 109 cm\(^{-1}\) (Ag). Thus, all the calculated Raman frequencies can be identified in our measurements, and the measured frequency bands match the averaged calculated values quite well (cf. figure 10). The origin of the deviations between measured and computed frequencies lies in the difference between measured cell parameters and the computed equilibrium unit cell parameters of α-Ga that are used in the calculations. For example, a shift of the shortest Ga-Ga distance from 2.55 Å to 2.46 Å generates a frequency shift from 236 to 254 cm\(^{-1}\) in the Ag mode.

### 3.5. Ga films deposited on Sn films at 25 °C

After Sn and Ga depositions at 25 °C, the three-region samples (cf. section 2.1) show only the reflection of β-Sn in the x-ray powder patterns for the Ga/\(\)Sn region. However, the refined lattice constants of β-Sn covered with gallium yield a smaller unit cell compared to the values refined from the sample area with pure tin, the latter being close to the known crystal data of the bulk \(\beta\)-Sn structure (cf. table 3). This suggests that, during gallium deposition, a \(\beta\)-Sn\(\)Ga solid solution is formed, which agrees very well with the Sn–Ga phase diagram, where \(\beta\)-Sn can dissolve up to 4.3 wt\% of Ga at room temperature \(\text{(Sn}_{0.93}\text{Ga}_{0.07})\). The refined lattice constants satisfactorily match the lattice constants of \(\text{Sn}_{0.95}\text{Ga}_{0.07}\). In the third sample region, where only gallium had been deposited on sapphire, an amorphous gallium film was obtained like during the pure gallium deposition described in subsection 3.1.

Surprisingly, upon cooling the sample, the amorphous Ga phase located on the Ga/\(\)Sn sample region transforms into a single phase \(\beta\)-Ga structure at around –60 °C, which is then stable down to –190 °C next to the \(\beta\)-Sn\(\)Ga phase. The refined \(\beta\)-Ga/\(\beta\)-Sn\(\)Ga ratio is around 50/50 wt\%. The lattice parameters of the \(\beta\)-Ga allotrope at –190 °C are presented in table 3. The refined lattice constants are slightly larger than the values for the pure \(\beta\)-Ga films suggesting that \(\beta\)-Ga may also contain a small amount of tin. When heating the sample to 25 °C, we observe a transformation of the \(\beta\)-Ga phase back into the amorphous state at around –20 °C (see figure SI-8), reminiscent of the phase transformations between the amorphous state and the \(\beta\)-Ga allotrope in subsection 3.1. Repeating the cooling + heating cycle yields the same structural evolution as the first thermal cycle. Figure 4 presents the allotrope formation during deposition as well as for the cooling + heating cycles of the Ga/\(\)Sn experiments (see top part, visualization analogous to figure 3).
Table 3. Lattice parameters and crystal sizes of Ga films deposited on Sn (Ga//Sn), together with the corresponding literature values, for comparison. For notation, cf. table 2.

| phase          | $T_{\text{measure}}$ | $T_{\text{deposit}}$ | a     | b     | c     | $\beta$ | $\rho_{\text{crys}}$ | $\lambda$ | References |
|----------------|----------------------|-----------------------|-------|-------|-------|---------|----------------------|-----------|------------|
| $\beta$-Sn(Ga) | 25                   | 25                    | 5.8003(8) |       |       | 3.1753(5) | 143                  |           |            |
| $\beta$-Ga     | $-190$               | 25                    | 2.7795(4) | 8.076(2) |       | 3.3365(6) | 92.07(2)             | 6.19      | 97         |
| $\alpha$-Ga    | $-190$               | $-190$                | 4.513(1) | 7.656(1) |       | 4.533(1) | 5.91                 | 41        |            |
| $\beta$-Sn     | $-190$               | $-190$                | 5.8104(9) |       |       | 3.1676(6) | 7.37                 | 29        |            |
| $\beta$-Sn(Ga) | 25                   | $-190$                | 5.7919(7) |       |       | 3.1725(4) | 206                  |           |            |
| $\beta$-Sn     | 20                   |                       | 5.8308  |       |       | 3.181    | 7.29                 |           | [45]       |
| $\beta$-Sn     | $-75$                |                       | 5.821   |       |       | 3.171    |                      |           | [45]       |
| Sn$_{0.93}$Ga$_{0.07}$ | 21          |                       | 5.785   |       |       | 3.170    | 7.22                 |           | [35]       |

In contrast, the amorphous Ga that had been deposited directly on sapphire but as isolated droplets far from the Ga//Sn sample region transforms during cooling into the $\beta$-Ga allotrope, just as we had seen in subsection 3.1 for the case of depositing only gallium at 25 °C. This indicates that the nearby presence of tin in the deposit prepared at 25 °C favors the formation of the $\beta$-Ga allotrope over the $\beta$-Ga allotrope.

An explanation can be found by studying the SEM images of the samples, presented in figure 11(a). At first sight, the Ga//Sn film looks similar to the gallium film deposited at 25 °C, where isolated droplets of different sizes are formed. But the droplets are larger in size (up to 3 μm) and not really spherical. Nearly on top, these droplets show a faceted structure, which looks like a cap. Furthermore, the element dependent contrast visible in the ESB image in the middle of figure 11(a) demonstrates that the lighter caps consist of tin and the residual droplet contains mostly gallium, because the higher electron density of tin atoms compared to the one of gallium atoms results in a brighter image. Furthermore, the pure tin films demonstrate that the tin deposits exhibit crystalline facets in contrast to the amorphous Ga droplets. Thus, the gallium deposits on tin grow as spherical droplets with a crystalline faceted tin cap that contains a few wt% Ga. Further insight into this process can be gained from the SEM images of the pure tin films (bottom of figure 11(a)) which had served as the substrates for the gallium deposition. Deposition of tin alone already produces isolated faceted polycrystalline droplets with sizes from 5 nm up to 2 μm on sapphire substrates but no dense film cover of the substrate. These crystalline tin droplets were then absorbed by gallium during the growth process forming tin cap gallium droplets. Since the crystalline tin deposits exhibit the $\beta$-Sn structure - which can even dissolve some small wt% Ga (cf. [35]) - , they can serve as heterogeneous nucleation centers for the structurally closely related $\beta$-Ga allotrope at low temperatures during the cooling + heating cycles. Furthermore, it cannot be excluded, that a small amount of tin present in $\beta$-Ga supports the nucleation of this allotrope.

3.6. Ga films deposited on Sn films at $-190$ °C

Using the three-region method, both tin and subsequently gallium were deposited on sapphire at $-190$ °C. The x-ray pattern of the Ga//Sn region of the sample exhibits the reflections of $\beta$-Sn and $\alpha$-Ga structures at $-190$ °C, with an $\alpha$-Ga/$\beta$-Sn amount ratio of ca. 50/50 wt% (cf. table 3). Upon heating, the two crystalline phases remain stable up to around 20 °C. However, at 25 °C $\alpha$-Ga transforms into the amorphous state, and by subsequent cooling the $\alpha$-Ga allotrope forms again near 20 °C (cf. also figure SI-9). Note that this contrasts with the behavior of the pure Ga deposit at $-190$ °C in subsection 3.4, where $\alpha$-Ga was stable up to the melting point but then transformed into the $\beta$-Ga allotrope from the melt. During this process, the $\beta$-Sn phase dissolves a small amount of gallium forming a $\beta$-Sn(Ga) solid solution, demonstrated by the decrease in lattice parameters measured at 25 °C compared to those of the pure $\beta$-Sn phase right after deposition at $-190$ °C. This suggests that the presence of the Sn–Ga alloy caused the amorphization of the $\alpha$-Ga structure already near room temperature. Moreover, the corresponding Rietveld refinements show increased crystallite sizes for the $\beta$-Sn(Ga) alloy, as well as the $\alpha$-Ga allotrope formation after cooling. The lattice parameters of $\alpha$-Ga remained unchanged. The crystal parameters obtained by these refinements are presented in table 3. A repetition of the heating + cooling cycle produced the same results.

Figure 11(b) shows SEM images of the Ga//Sn region deposited at $-190$ °C together with the pure tin region of the sample. As was the case for pure Ga deposition at $-190$ °C in subsection 3.4, the deposition of Sn at $-190$ °C produces rough, dense films, which cover the complete substrate. The topography of the tin surface looks like an accumulation of roundish splashes of paint, which are then smoothed out by covering the surface with gallium in the second deposition stage. The corresponding ESB image shows tin (lighter contrast) only as a few isolated areas on top of or adjacent to the Ga particles, suggesting that most of the tin still lies below the gallium film.
A summary of the structural evolution of the films deposited at 25 °C and –190 °C during the heating + cooling cycles of the Ga//Sn system is given in figure 4. The color scheme is analogous to that for the pure gallium deposition (cf. figure 3 and sections 3.1–3.4).

3.7. Ga-Sn films (20 wt% Sn) co-deposited on a sapphire substrate at 25 °C

Gallium and tin were deposited together onto sapphire substrates with a ratio of 20 wt% Sn to 80 wt% Ga. This simultaneous deposition of both elements forms light grey films of isolated droplets at 25 °C. The x-ray powder patterns of the films show reflections corresponding to a crystalline β-Sn(Ga) solid solution, while the gallium phase is x-ray amorphous at 25 °C. When cooling, the β-Sn(Ga) phase remains unchanged down to –190 °C. However, according to the powder patterns, a part of the amorphous gallium transforms to the β-Ga allotrope at –50 °C and the remainder to the γ-Ga allotrope at –60 °C, respectively. The two metastable Ga allotropes persist down to –190 °C, and the phase content of β-Ga and γ-Ga is 55 wt% and 25 wt%, respectively. The refined lattice parameters are given in table 4. Upon heating, both phases transform back into the amorphous state, with the transformation occurring at –30 °C for the γ-Ga phase and at around –10 °C for the β-Ga phase. In contrast, the β-Sn(Ga) is stable in the complete temperature range (see figure SI-10). Additional cooling + heating cycles showed the same structural evolution for the gallium fraction of the deposit (cf. figure 5 for allotrope formation analogous to figure 4). The refined lattice constants of the β-Sn(Ga) solid solution are only slightly smaller than
the values of pure $\beta$-Sn in the literature, supporting the existence of the $\beta$-Sn($\text{Ga}$) solid solution with a very low gallium content, estimated to ca. 1 wt% Ga (cf. table 4). Furthermore, the lattice constants of $\beta$-Ga and $\gamma$-Ga are slightly increased compared to the refined values of pure gallium films, which suggests that these films may also contain a small amount of tin.

The topography of the co-deposited Ga-Sn films was investigated by SEM and the corresponding images are presented in figure 12(a). After deposition, the surface structure consists of spherical droplets of gallium (up to 1.5 $\mu$m), only some of which are capped by crystalline tin, as can be seen in the ESB images. The faceting of these caps is less pronounced than for those found in the Ga/$\alpha$-Sn samples. Thus, the co-deposition leads to partial separation of the two components: spheres and capped spheres. The existence of the non-capped Ga particles is most likely due to the low fraction of tin (only 20 wt% Sn) compared to the Ga/$\alpha$-Sn experiments, where Ga and Sn were deposited in approximately equal amounts. Referring to the Ga/$\alpha$-Sn experiments, we assign the $\beta$-Ga phase to the capped spheres and the $\gamma$-Ga phase to the round spheres, respectively.

3.8. Ga-Sn films (20 wt% Sn) co-deposited on a sapphire substrate at –190 °C

The co-deposition of tin and gallium onto a substrate at –190 °C directly leads to crystalline samples. The in situ measured x-ray diffraction patterns prove the formation of the $\beta$-Sn(Ga) solid solution and the $\alpha$-Ga allotrope side by side ($\alpha$-Ga: 80 wt%, $\beta$-Sn(Ga) 20 wt%). We note that the Sn-Ga alloy occurs already at –190 °C and the gallium content seems to be very low, as indicated by the very small shrinking of the lattice constant. On the other hand, the lattice constants of $\alpha$-Ga are significantly increased compared to the pure gallium deposition, perhaps due to a small amount of tin also being present in the $\alpha$-Ga phase.

| phase            | $T_{\text{measure}}$ | $T_{\text{deposit}}$ | a     | b     | c     | $\beta$ | $\rho_{\text{crys}}$ | $\lambda$ |
|------------------|----------------------|-----------------------|-------|-------|-------|--------|------------------------|-----------|
| $\beta$-Sn(Ga)   | 25                   | 25                    | 5.8091(7) | 3.1810(5) | 116   |
| $\beta$-Ga      | –190                | 25                    | 2.7807(6) | 8.065(2)  | 3.332(9) | 92.03(1) | 6.20                    | 68        |
| $\gamma$-Ga     | –190                | 25                    | 10.683(4) | 13.690(5) | 5.133(2) | 6.17    | 150                    |
| $\alpha$-Ga     | –190                | –190                  | 4.5326(7) | 7.6919(7) | 4.5490(8) | 5.84    | 36                     |
| $\beta$-Sn(Ga)  | –190                | –190                  | 5.8052(7) | 3.1727(8) | 32     |

The topography of the co-deposited Ga-Sn films was investigated by SEM and the corresponding images are presented in figure 12(a). After deposition, the surface structure consists of spherical droplets of gallium (up to 1.5 $\mu$m), only some of which are capped by crystalline tin, as can be seen in the ESB images. The faceting of these caps is less pronounced than for those found in the Ga/$\alpha$-Sn samples. Thus, the co-deposition leads to partial separation of the two components: spheres and capped spheres. The existence of the non-capped Ga particles is most likely due to the low fraction of tin (only 20 wt% Sn) compared to the Ga/$\alpha$-Sn experiments, where Ga and Sn were deposited in approximately equal amounts. Referring to the Ga/$\alpha$-Sn experiments, we assign the $\beta$-Ga phase to the capped spheres and the $\gamma$-Ga phase to the round spheres, respectively.

3.8. Ga-Sn films (20 wt% Sn) co-deposited on a sapphire substrate at –190 °C

The co-deposition of tin and gallium onto a substrate at –190 °C directly leads to crystalline samples. The in situ measured x-ray diffraction patterns prove the formation of the $\beta$-Sn(Ga) solid solution and the $\alpha$-Ga allotrope side by side ($\alpha$-Ga: 80 wt%, $\beta$-Sn(Ga) 20 wt%). We note that the Sn-Ga alloy occurs already at –190 °C and the gallium content seems to be very low, as indicated by the very small shrinking of the lattice constant. On the other hand, the lattice constants of $\alpha$-Ga are significantly increased compared to the pure gallium deposition, perhaps due to a small amount of tin also being present in the $\alpha$-Ga phase.

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Upon heating to room temperature, the complete sample transforms into the x-ray amorphous state at around 25 °C; in practice, it can take several hours (up to one day) until all reflections of the β-Sn(Ga) phase have vanished from the x-ray pattern. During the subsequent cooling, the sample transforms back into the mixture of the β-Sn(Ga) and α-Ga phases near 20 °C, and these remain stable down to −190 °C (see also figure SI-11, figure 5). The refined lattice constants are presented in table 4. The lattice constants of β-Sn(Ga) slightly decrease during this cycle, which indicates an increasing Ga content in the alloy. On the other hand, the lattice constants of α-Ga also increase, which suggests a slight uptake of tin. Thus, an exchange of Sn/Ga occurs during this process without a significant change in the crystallite sizes. According to the Ga-Sn phase diagram, the solubility of gallium in tin decreases with decreasing temperature, which is verified by the refined lattice constants of the β-Sn(Ga) alloy formed at −190 °C.

The SEM images of figure 12(b) show flat rough dense films with a casting-like topography. Tin is not really visible in the ESB mode. Thus, in these co-deposited films a homogeneous distribution of the elements on the nanometer scale is present. This differs from the Ga//Sn samples deposited at −190 °C. During the co-deposition the elements are mixed on atomic level and the overall amount of tin in the films is at 20 wt% Sn. This fraction is not too far away from the eutectic composition in the Sn-Ga phase diagram (13.7 wt% Sn) which melts at 21 °C. Thus, the melting of the complete sample at 25 °C seems to be possible.

Summaries of the structural evolution during the cooling + heating cycles after co-deposition at 25 °C and −190 °C, respectively, are shown in figure 5.

3.9. Equations of state of the gallium allotropes

For all functionals that we used in the CASTEP and VASP calculations of the equations of state $E(V)$, the allotrope $β'$-Ga exhibits the smallest minimum energy $E_{\text{min}}$, followed by the α-Ga and β-Ga allotropes (see figure 13). However, we note that the minimum energies of the allotropes α-Ga, β-Ga and $β'$-Ga, are quite close, and we cannot assign a final definitive energy ranking among these three allotropes, considering the overall limitations of the ab initio calculations. In contrast, the γ-Ga and δ-Ga allotropes of gallium possess significant higher minimum energies $E_{\text{min}}$. Since the unit cell volume and number of atoms/unit cell greatly vary among the allotropes, we have repeated the calculations for the supercells $4 \times 2 \times 4$ for α-Ga, $6 \times 3 \times 6$ for β-Ga and $3 \times 3 \times 6$ for $β'$-Ga, containing a larger number of atoms, and again compared the energies per gallium atom. We found that the increase of the supercell dimensions of gallium allotropes did not change the order of the minimum energies.

The optimized unit cell parameters of the $β'$-Ga allotrope differ noticeably from the refined parameters of the x-ray patterns, beyond what we typically observe when comparing theoretical and experimental cell parameters. The corresponding cell parameters compared to the $β$-Ga values are shown in table 5. Both the measured and calculated $β'$-Ga structures are derivatives of the $β$-Ga structure, where for the optimized $β'$-Ga structure the b-axis is shortened and the a-axis is expanded compared to $β$-Ga, and vice versa for the x-ray refined $β'$-Ga structure (cf. figure SI-12). This issue illustrates the softness of this gallium structure and exposes the difficulties finding the real minimum structure, both in the experiment and in calculations.

In the literature, several DFT studies of the crystal structure and the equation of state $E(V)$ of the experimentally known gallium allotropes exist [46-49]. Most of them had been performed using a LDA.
exchange-and-correlation functional more than a decade or two ago. In these studies, the lowest energy minimum of the $E(V)$ curves corresponded to the $\alpha$-Ga phase [46, 48], which differs from our results.

To clarify this discrepancy, we have verified the validity of our results, in particular that the lowest energy minimum of the $E(V)$-curves does not correspond to the $\alpha$-Ga phase, by performing VASP based calculations for the $\alpha$-Ga, $\beta$-Ga and $\beta'$-Ga allotropes with a variety of exchange-and-correlation functionals, LDA (Ceperley-Alder), GGA (PW91) and PAW PBE, and different cut-off energies for the plane waves (cf. figure SI-13). We find that the minimum of the $E(V)$-curve for the $\beta'$-Ga allotrope is lower than the one for $\beta$-Ga only when we use the LDA functional together with a rather small cut-off for the plane waves.\(^4\) But even then the $\beta'$-Ga allotrope is the lowest one in energy.

From the $E(V)$ curves (or, equivalently, from the $H(p)$ curves shown in figures SI-14 and SI-15 of the SI), we can compute the transition pressures for CASTEP (VASP) based calculations, between the $\beta'$-Ga/$\beta$-Ga and $\alpha$-Ga/$\beta'$-Ga phases, 8.8 GPa (2 GPa) and $-2.5$ GPa ($-2.5$ GPa), respectively. This value can be compared with the hydrostatic pressure inside a spherical droplet (due to the surface tension). Using the known relation between the pressure $P$, the surface tension $\sigma$, and the radius $r$ describing this effect, $P = 4\sigma / r$, and the reference data on the surface tension $\sigma = 0.74$ Nm$^{-1}$ of liquid gallium at the temperature 700 K (427 °C) [50], one can obtain a diameter $d \approx 0.7$ nm (3 nm) of the droplets corresponding to the critical pressure $P = 8.8$ GPa (2 GPa) of the possible $\beta$-Ga/$\beta'$-Ga phase transformation of gallium. This result indicates that transformations might occur between the $\beta$ and $\beta'$ allotropes at the initial stage of the gallium droplet’s crystallization.

### 3.10 MD simulations and computation of Raman spectra of the Ga allotropes

For further insights into the dynamical behavior of the different Ga-allotropes, we have performed molecular dynamics (MD) calculations using the VASP code with NVE ensembles, with energies corresponding to several temperatures in the range between 10 K ($-263$ °C) and 700 K (427 °C).

\(^4\) While this demonstrates that the ranking of the energy minima for different gallium allotropes may depend on the choice of the pseudo-potential and number of plane waves used, it appears to be clear that, in particular, one should avoid a low cut-off of the energy of the plane waves. We strongly suspect that the definitive determination of the correct ranking in energy of the elemental gallium allotropes will require going beyond the standard DFT functionals, taking e.g. electron-phonon interactions, spin-based interactions, and/or higher-order electron-electron screening into account.

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**Table 5.** The optimized unit cell parameters, $a$, $b$, $c$ and $\beta$, for the $\beta$-Ga and $\beta'$-Ga allotropes obtained using the CASTEP code, with an ultra-soft pseudo-potential Ga_00PBE.usp and a PBE exchange-and-correlation functional, compared to the refined values of $\beta'$-Ga via XRD and of $\beta$-Ga [5] (doubled cell parameter $a$ is given in parentheses, for comparison with $\beta'$-Ga).

| Phase               | $a$ / Å  | $b$ / Å  | $c$ / Å  | $\beta$ /° |
|---------------------|----------|----------|----------|-------------|
| $\beta$-Ga (refined by XRD) | 5.200(1) | 8.446(2) | 3.314(1) | 87.11(2)   |
| $\beta$-Ga (calc. by CASTEP) | 6.0015 | 7.4884 | 3.2631 | 90.00       |
| $\beta$-Ga (calc. by CASTEP) | 2.9480 | 7.8583 | 3.1026 | 90.00       |
| $\beta$-Ga [5]     | 2.766 (5.532) | 8.053 | 3.333   | 92.03       |

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**Figure 14.** (a) Mean squared displacement $\delta^2$ of the atoms in $\alpha$-Ga as function of temperature $T$, measured over a simulation time of 8.4 ps. Note the large non-linearity. (b) Temperature dependence of the root mean squared deviation $\delta(T) = \sqrt{\langle\delta^2(T)\rangle}$ of the $\alpha$-Ga allotrope, which essentially corresponds to the amplitude of the vibrations in the system for temperatures up to the melting point (cf. figure 15, where we see that, at room temperature, essentially no diffusion takes place in $\alpha$-Ga).
Figure 15. Time dependence of mean squared displacement $\delta^2(t)$ of gallium atoms for $\alpha$-, $\beta$- and $\gamma$-allotropes at 78 K (−195 °C) and 303 K (30 °C).

Figure 14(a) shows the mean squared displacement $\delta^2(T)$ of the atoms in $\alpha$-Ga, which exhibits a rather large nonlinearity as function of temperature $T$. This suggests an on average relatively weak bonding between gallium atoms, and a related loss of long-range atomic order already at room temperature, which is consistent with its relatively low melting temperature $T_m(\alpha) \approx 303$ K (29.8 °C). From figure 14(b), we see that at about 300 K (27 °C), we have $\delta \approx 0.25 \AA$, which corresponds to the 10% of the nearest-neighbor distance in crystalline gallium, at which melting should set in according to the classical Lindemann criterion [51]. Another feature extracted from the MD simulations, which is related to the mobility of the Ga atoms, are the large values of $\beta$ at zero frequency ($\nu = 0$) for the temperatures 500 K (227 °C) and 700 K (427 °C) (cf. figure SI-16). This again indicates a large Ga atom mobility both in the liquid state of the material and already close to the melting temperature (cf. also the plot of $\delta^2(T, t)$ versus time $t$ in figure SI-17), since the value of the vibrational density of states $G$ at the frequency $\nu = 0$ may be used to estimate the coefficient of self-diffusion of a material [43].

For comparison, we consider the mean squared displacement as function of time (cf. figure 15) derived from MD simulations at two different temperatures (78 K and 303 K −195 °C and 29.8 °C), together with the pair distribution functions (cf. figure SI-18 in the SI), for the $\alpha$-Ga, $\beta$-Ga, and $\gamma$-Ga allotropes, respectively. From these, we see that especially the $\gamma$-Ga phase is quite soft structurally, already at liquid nitrogen temperatures: the mean squared displacement is very large indicating very mobile Ga atoms, and the pair distribution function exhibits only extremely broad peaks as one would expect from a liquid, even at 78 K. In contrast, the $\alpha$-Ga and $\beta$-Ga phases are relatively stable, exhibiting an essentially constant mean squared displacement as function of time for both temperatures, although here, too, the peaks in the pair distribution function are quite broad even at 78 K and become rather washed out at 303 K.

In summary, the rather large mobility of the gallium atoms may facilitate structural phase transformations, result in large coefficients of thermal expansion and a low melting point, and cause the noticeable change in the phonon density of states as function of temperature.

Finally, we performed DFT based calculations to compute the Raman frequencies for the $\alpha$-, $\beta$-, $\beta'$-, $\gamma$-, and $\delta$-Ga allotropes, using the CASTEP code (cf. tables SI-1 and SI-2). The calculated results presented in figure 16 correspond to the following densities $\rho$ of the gallium allotropes: 5.99 g cm$^{-3}$ ($\alpha$-Ga), 6.40 g cm$^{-3}$ ($\beta$-Ga), 6.40 g cm$^{-3}$ ($\beta'$-Ga), 6.20 g cm$^{-3}$ ($\gamma$-Ga). We note that for the purpose of verifying the general shape and robustness of the computed Raman spectra, these calculations were also performed with supercells of the $\alpha$-Ga structure and with other functionals. As a consequence, the Ga-Ga distances are slightly different, which noticeably influences the computed frequencies. For the comparison with the measured Raman bands, we computed the average over the calculated Raman frequencies, for each of the six modes (cf. table SI-1). The band of the experimental Raman spectrum at the frequency $\nu = 250$ cm$^{-1}$ is attributed to the $\alpha$-Ga phase due to the closeness to the strongest calculated frequency at $\nu = 252$ cm$^{-1}$. This conclusion is also in agreement with the shortest Ga - Ga interatomic distance found in the $\alpha$-Ga phase (cf. also figures SI-19 and SI-20). The experimental band at 220/193 cm$^{-1}$ can, in principle, also be attributed to the $\alpha$-Ga phase (two calculated
Raman frequencies are equal to $219 \text{ cm}^{-1}$ and $201 \text{ cm}^{-1}$, and similarly the band at the frequency $\nu = 149 \text{ cm}^{-1}$ to the calculated one of the $\alpha$-Ga phase at $154 \text{ cm}^{-1}$. The remaining two calculated frequencies, $\nu = 89 \text{ cm}^{-1}$ and $\nu = 109 \text{ cm}^{-1}$, are located near the obtained intensity increase in experimental Raman spectrum at approximately $\nu = 100 \text{ cm}^{-1}$ (cf. figure 10). For further discussions of the calculations of the theoretical Raman spectra, we refer to the SI.
4. Discussion

4.1. Allotrope formation

We have investigated the stability ranges and phase transitions of gallium allotropes, both in pure Ga and in Ga-Sn alloys, in films deposited via femto-PLD technique as well as during subsequent cooling + heating cycles, as function of the initial deposition temperature. Figures 3–5 provide a comprehensive overview over the structural evolution of the various samples.

Figure 17 summarizes these results for the pure gallium deposition and annealing experiments in form of a deposition-temperature-annealing-schedule (DTAS) phase diagram. It shows the phase evolution of the gallium deposits through two cooling + heating cycles. In contrast to a standard phase diagram that depicts the thermodynamically stable bulk phase (after infinite relaxation times at the given values of the thermodynamic parameters; here: the temperature, with pressure fixed at 10⁻⁸ mbar), the DTAS diagram captures, at finite observation times, both the dependence on initial (deposition) conditions and the preferred fast transformations among metastable phases. As a rough summary: for deposition temperatures below –60 °C, only α-Ga is formed; above –60 °C, the β-Ga allotrope crystallizes from an amorphous phase that is generated either directly or after heating to room temperature; and in a small range of deposition temperatures (–20 °C to –60 °C), the β'-Ga and γ-Ga allotropes are formed but prove to be unstable when heated to room temperature. The crystallization of the β'-Ga and γ-Ga allotropes (between –20 °C and –60 °C) only during the deposition process highlights the difference in the formation of solids by a gas phase deposition compared to an annealing procedure. In the former one, the solid is built up from the gas phase by adding one atom at a time, while the latter one corresponds to a re-arrangement of the atoms inside an existing solid at a specific annealing temperature. In our case, these two procedures lead to different (meta)stable phases, all of which are kinetically stable, on the time scale of the experiments, at the temperature where the deposition or annealing, respectively, take place. Due to the different formation kinetics of these two procedures, we are able to access different phases of gallium at the same thermodynamic boundary conditions, i.e. at the same temperature and pressure, on the finite time scale of the experiment - only on essentially infinite time scales, a transformation of the metastable phase(s) into the thermodynamically stable phase would occur.

Among the four well-known crystalline gallium structures at ambient conditions, α-Ga is the thermodynamically stable allotrope. Its structure consists of distorted honeycomb layers of Ga-atoms that contain Ga-Ga dimers, which are stacked along the a-axis (cf. figure 1). Usually this allotrope is spontaneously formed in bulk from a melt upon introduction of a seed crystal, or by exposure of the melt to external shocks or...
The metastable $\beta$-Ga, $\gamma$-Ga, and $\delta$-Ga allotropes crystallize from the undercooled melt at around $-16^\circ \text{C}$, $-35^\circ \text{C}$, and $-19^\circ \text{C}$, respectively.

Historically, when attempting to explain the appearance of polymorphism in materials science, F W Ostwald had suggested that a system evolves step by step to the energetically / thermodynamically lowest state [52]. This would mean that the least stable polymorph crystallizes first from the melt (Ostwald’s rule), which usually is also the solid phase with the lowest density. Of course, Ostwald’s rule lacks a firm justification because no thermodynamic reason exists, why the system should not directly transform to the thermodynamic groundstate. This forces us to turn to kinetic consideration to explain the sequence of metastable phases one observes. In particular, we note that kinetic arguments suggest that the phase that is most likely to nucleate inside the starting phase, is the one which should form first. Assuming all other features relevant to the nucleation kinetics being equal (e.g., no seeds of other phases already present, no preferred structural relations such as group-subgroup relations between phases, etc), this phase would be the one which is closest in density to the starting phase in which the nucleation takes place, since its nuclei would possess the lowest surface energy associated with the interface between the nuclei and the surrounding starting phase. The first starting phase in such a phase formation sequence is typically the melt, but it can also be an amorphous phase in which the first nucleation and crystallization takes place; we note that such amorphous phases usually have a density lower than those of crystalline solid phases and slightly higher than that of the liquid phase. Examples are the formation of low-density phases of MgF$_2$ [53] or K$_3$N [54] at very low temperatures via crystallization inside an amorphous film that had been deposited from the gas phase. We note that this kinetic argument, which favors the lowest density phase to be the first to crystallize from the (slightly) undercooled melt, leads to the same result as Ostwald’s rule as long as the higher density modifications are also the lower ones in energy.

However, $\alpha$-Ga ($\rho = 5.91 \text{ g cm}^{-3}$) is an unusual case since it has the lowest density of all the gallium allotropes (cf. table 2) – even lower than the liquid ($\rho = 6.10 \text{ g cm}^{-3}$ at 30 °C) and the amorphous phase ($\rho = 6.14 \text{ g cm}^{-3}$ at $-16^\circ \text{C}$) [3] - but nevertheless is the most stable one experimentally (although the theoretical calculations suggest otherwise; cf. the E(V)-curves in figure 13). This conflict is the origin of the unexpected order of appearance of the gallium allotropes we obtain in our films, as function of deposition temperature. Quite generally, we note that the lower the deposition temperature from the gas phase, the higher the effective cooling rate, which, combined with the reduced diffusion rate at lower temperatures, results in less dense deposits. Under these conditions, the allotrope with the lowest density, $\alpha$-Ga, is formed only at lower deposition temperatures between $-60^\circ \text{C}$ and $-190^\circ \text{C}$, but is not produced if the deposition temperature is above $-60^\circ \text{C}$. Of course, once the $\alpha$-Ga allotrope has been formed, then it is stable at all temperatures below the melting point (cf. figure 17).

At higher deposition temperatures, between $-60^\circ \text{C}$ and $-20^\circ \text{C}$, the $\beta$-Ga and $\gamma$-Ga modifications crystallize. These allotropes have higher densities and their formation can be considered to follow Ostwald’s rule, based on our above observations that nucleation in a frozen random deposit at low temperatures corresponds to nucleation in a melt close to the melting temperature, and by furthermore taking into account that lower deposition temperatures generate less dense deposits. Thus, at the lowest deposition temperature the least dense polymorph $\alpha$-Ga is formed, followed by $\gamma$-Ga and $\beta$-Ga with their higher densities, at higher deposition temperatures (cf. figure 17). This behavior has also been observed in the preparation of AgNO$_3$ and InCl, for example, using the low-temperature atomic beam deposition method [55, 56]. From an amorphous deposit generated at very low temperatures, the modification with the lower density, which was the known high-temperature polymorph, crystallizes first upon raising the temperature, and then transforms during further heating to the thermodynamically stable room temperature modification. Finally, the HT-polymorph is recovered at elevated temperatures. Clearly, the formation of the $\beta$-Ga and $\gamma$-Ga allotropes at intermediary deposition temperatures proceeds in a similar fashion.

We note that the difference in density of the $\beta$-Ga and $\gamma$-Ga allotropes is so small that it is impossible to predict their order of appearance based on density alone. Interestingly, above $-20^\circ \text{C}$ these two allotropes both transform to the amorphous state. On the one hand this behavior reflects the metastability of these allotropes, which prevents them from remaining stable as a macroscopic crystalline phase up to the actual melting point of gallium, and thus favors the formation of an amorphous phase similar to a frozen-out undercooled melt - recall that the temperature ($-20^\circ \text{C}$) is near but below $T_{\text{mel}}$, and that the system starts the transformation to the amorphous state from a solid phase (cf. figure 17). On the other hand, the amorphous phase close to the melting point has a higher density than the thermodynamically stable $\alpha$-Ga phase, which strongly impedes an (unperturbed) nucleation of the $\alpha$-Ga phase inside the amorphous state. The appearance of an (at least x-ray) amorphous state is thus not completely surprising, where one cannot exclude the possibility that extremely tiny nano-crystals of $\beta$-Ga or $\gamma$-Ga may still exist in the amorphous phase. This phase appears in the shape of spherical amorphous droplets, which supports our analysis that this amorphous phase is a metastable

\footnote{For the purpose of this discussion, we do not distinguish between the $\beta$-Ga and the closely related $\beta'$-Ga allotropes.}
intermediary state between the liquid phase and the crystalline \( \beta \)-Ga and \( \gamma \)-Ga allotropes. Additional support comes from the fact that spherical particles frequently appear during the cooling of bulk molten metals, minimizing their surface energy in the process [57].

Since the density of molten gallium is higher than the density of the \( \alpha \)-Ga allotrope but lower than the density of the other allotropes, the formation of the \( \beta \)-Ga, \( \gamma \)-Ga, and \( \delta \)-Ga allotropes from the under-cooled melt is accompanied by an increase in density, and thus corresponds to the ‘normal’ crystallization process.

In contrast, for a direct formation of \( \alpha \)-Ga from the melt, the density must be decreased requiring an implausible large volume fluctuation: Using the standard formula for fluctuations in the volume/atom, \( \langle (\Delta v)^2 \rangle = \frac{k_B T \gamma}{N^2} \), and assuming that ca. 1000 atoms need to be involved in the formation of a stable nucleus of a phase, we find at room temperature and with a compressibility of \( \gamma \approx 2 \text{ Mbar}^{-1} \), after taking the square root of the variance, that fluctuations of the size of roughly \( 1/30 \text{ Å}^3 \) in the volume per atom \( v = \frac{V}{N} \) are to be expected for a group of 1000 atoms. Now, the change in volume/atom needed to achieve the jump by about three percent in density from 6.14 g cm\(^{-3}\) for \( \alpha \)-Ga is about \( 1/3 \text{ Å}^3 \), because the volume/atom in solid Ga is roughly \( 10 \text{ Å}^3 \), requiring a volume fluctuation that is at least four orders of magnitude less likely than a standard thermodynamic fluctuation. Furthermore, no mechanism besides the fast growth of the nucleus exists, which can prevent back-fluctuations into the higher-density liquid or amorphous phase (such back-fluctuations have been seen in e.g. simulations of homogeneous nucleation of ice in super-cooled water [58], another system where the density of the solid phase is smaller than the one of the melt at the phase transition point). In contrast, the higher-density metastable Ga allotropes are much closer in density (\( \beta \)-Ga, \( \gamma \)-Ga, and \( \delta \)-Ga differ by only one percent in volume/atom from the amorphous phase), and once a nucleus is formed, the breaking of bonds with the surrounding amorphous matrix will eliminate the effective negative pressure the nucleus experiences in the amorphous matrix, making a back-fluctuation highly unlikely.

Thus, it seems that the kind of local volume expansion needed for the formation of the \( \alpha \)-Ga phase will only occur during the nucleation stage, if the crystallization starts from the liquid melt and is furthermore assisted by external influences such as heterogeneous nucleation, large amplitude sound waves, or by providing a seed of the \( \alpha \)-Ga phase, but not via homogeneous nucleation from a high-density solid deposit. Due to this unusual combination of liquid and solid allotrope densities and their energetic ranking, a kinetic barrier appears to exist between the energy landscape regions associated, in the solid state, with \( \alpha \)-Ga on the one side and those with the \( \beta \)-Ga, \( \gamma \)-Ga and \( \delta \)-Ga allotropes on the other side, as no direct transitions have been observed between these two sides in the solid state during any of our experiments.

Furthermore, it seems that the difference of energy of formation of \( \beta \)-Ga and \( \gamma \)-Ga is so small that we often find \( \beta \)-Ga and \( \gamma \)-Ga together. This observation is also supported by our theoretical calculations of the E(V) curves (see section 3.9). Moreover, the experiments reveal \( \beta \)-Ga as more stable than \( \gamma \)-Ga: During the phase transitions into the amorphous state, of those gallium films that had been deposited at \(-40 \degree \text{C} \), the \( \beta \)-Ga allotrope disappears last among the crystalline allotropes when increasing the temperature. For the Ga-Sn films co-deposited at \( 25 \degree \text{C} \), the \( \beta \)-Ga allotrope is the first one that crystallizes and the last one that vanishes during the cooling and heating cycles, respectively. We note that, in all our experiments, no hint of a formation of the \( \delta \)-Ga allotrope was observed. As the \( \delta \)-Ga allotrope (at \(-19 \degree \text{C} \)) crystallizes in a very narrow temperature range that is close to the crystallization temperature of the \( \beta \)-Ga allotrope (\(-16 \degree \text{C} \)), the formation of the \( \delta \)-Ga allotrope may be suppressed in our films.

### 4.2. The \( \alpha \)-Ga alltrope

In our experiments, the \( \alpha \)-Ga allotrope crystallizes only in films deposited at low temperatures between \(-60 \) and \(-190 \degree \text{C} \). Figure 18 shows x-ray powder patterns (all measured at \( 25 \degree \text{C} \)) of three different \( \alpha \)-Ga samples deposited in this temperature range compared to the calculated line pattern of the bulk \( \alpha \)-Ga structure. Viewing the patterns in detail reveals a remarkable deviation of reflection intensities with regard to the intensities of the bulk \( \alpha \)-Ga structure. In particular, three reflections are noteworthy here: with decreasing deposition temperature, the reflections at around \( 30\degree \), \( 40\degree \) and \( 46\degree \) in 2\( \theta \) decrease, and the one at \( 40\degree \) almost disappears at \(-190 \degree \text{C} \). These variations of the intensity seem to be a continuous function of deposition temperature, and we believe that their origin is an increasing structural disorder in the gallium atom arrangement, with decreasing deposition temperature. We find that the variations of the intensities can be described by structure models that use additional degrees of freedom in the atomic parameters.

In a first step (called disorder model 1), the originally fixed x-parameter of the 8 f Ga site (original atom position \((0.0, 0.155, 0.081)\)), was allowed to be refined (with site occupation factor of one half, to take into account the doubled number of atom positions inside of the unit cell caused by the transformation of the 8 f to a 16 g site). In the second step (called disorder model 2), an additional Ga site (16 g) was added (starting atom position \((0,0,0)\)) and both sites were refined with an occupation factor of \( \frac{1}{2} \) in total. Figure 19 shows the crystal structures resulting from the two disorder models compared to \( \alpha \)-Ga. The corresponding crystal data are shown
Figure 18. X-ray powder pattern of α-Ga films deposited at low temperatures: −80 °C (green curve), −100 °C (blue curve), and −190 °C (red curve). Green line diagram: bulk α-Ga.

Figure 19. Schematic drawing of the disorder model 1 (middle) and model 2 (bottom) of the α-Ga structure. For comparison, we also show the α-gallium structure (top). (a) Two unit cells along the c-axis, with selected gallium bonds being highlighted. (b) One layer in the (011) ’plane’. The splitting of the layers (model 1) is indicated by yellowish bonds, and in model 2 the additional disorder inside of the layers is indicated by blue atoms.
in table SI-3, and the calculated x-ray patterns are shown in figure SI-21. With decreasing deposition temperature, the density decreases (lattice parameters expand) and the shortest Ga-Ga distances increase (cf. table SI-3). We note that the x-ray patterns of the samples deposited at −80 °C satisfactorily match those of the bulk α-Ga structure. But the refinement of the two free atom parameters of the 8 f Ga site results in a shift compared to the single crystal data, which corresponds to a distinct increase of the shortest bond length from 2.48 Å to 2.6 Å. The corresponding calculated x-ray pattern (cf. figure SI-21, green curve) shows reduced intensities of the reflections at 30° and 46° in 2θ. The x-ray pattern of the samples deposited at −100 °C can already be adequately refined by the first disorder model, while the samples deposited at −190 °C require the second disorder model. The corresponding changes in the x-ray patterns are also depicted in figure SI-21. The α-Ga structure consists of honeycomb layers in (100) of distorted hexagons stacked in [25/25]0 (see figure 19). The hexagons in the layers are oriented in one row (A) towards the −c direction and then in the following row (B) in the opposite direction, i.e. towards the +c direction, respectively (see figure 19(b)). The disorder model 1 describes a disorder along the a-axis and model 2 adds a disorder in the (100) layer - especially along [001] -, respectively. The model 2 consists of hexagons, which can be generated by an overlay of rows A and B of the α-Ga layers. The salient effect of this is the loss of the (200) and (002) reflections at 40° in 2θ. This also suggests that the bulk α-Ga structure has a limited stability range and, therefore, the amorphous state may be reached at very low temperatures. This result agrees very well with quenched condensation experiments, where amorphous gallium films were obtained at about −260 °C [25]. However, we note that it would be unusual if the thermodynamic minimum at zero temperatures, i.e. the ground state of gallium, were an amorphous phase, and thus the presence of the amorphous state is most likely due to limited observation times that are not sufficient for the system to reach global equilibrium, and transform into either α-Ga or some superstructure of e.g. β-Ga, such as the β-Ga structure.

Additional insights can be gained from the in situ Raman measurements of α-Ga. We recall that for the β-Ga, β-Ga, and γ-Ga allotropes, no discrete Raman bands were measured between 25 °C and −190 °C. This is different for the α-Ga allotrope, where four sharp Raman bands were detected at −190 °C, which are visible up to temperatures around 0 °C and then completely vanish at higher temperatures leaving only a broad background signal from 300 cm−1 to 100 cm−1. In the literature, Raman measurements of solid bulk α-Ga at room temperature are reported in just one publication [59]: the authors detected only one Raman band at 246 cm−1, which they attributed to the symmetric stretching vibration of the gallium atom dimers. Thus, it seems possible to measure a Raman band in gallium at room temperature using a specially prepared bulk material. Keeping in mind that (for metals) Raman is essentially a surface probe, we note that the literature result was obtained employing a smooth shiny surface of gallium, in contrast to the much rougher films in our experiments, which explains the difference in appearance between the bulk Raman spectra and those in our α-Ga films at room temperature.

The existence of sharp Raman bands for α-Ga films only at low temperatures can be understood as follows. Due to the low melting point of gallium (29.8 °C), it is very difficult to measure the Raman bands near room temperature. Furthermore, the energy input of the laser light causes additional local heating and thus complicates the Raman measurements even further (cf. [60]). With decreasing temperature, this thermal excitation of the lattice is reduced, making low-temperature Raman measurements feasible for all allotropes, in principle. But only α-Ga contains dimers that are connected in an asymmetric fashion to six further gallium atoms before the appearance of a bond distance gap of around 1 Å to the next neighbor atom shell (cf. figure 1 and figure SI-19). Thus, the relatively discrete vibration modes of the Ga atoms in the α-Ga phase are more easily detectable by Raman measurements compared to the other allotropes, which show a more continuous interatomic distance distribution. Thus, the presence of discrete Raman modes is the consequence of the Ga dimer and their relatively weak coupling to the lattice.

To assign the Raman bands to vibration modes we have performed theoretical calculation of the Raman frequencies using the CASTEP code (cf. section 3.10). The calculated frequencies of the Raman modes together with the frequencies of the experimental Raman spectrum for α-Ga allotrope are presented in figure 10. One finds a satisfactory agreement of the calculated and experimental results.

4.3. The new β-Ga allotrope

Upon cooling amorphous samples to temperatures below −40 °C, we always obtain the new crystalline β-Ga allotrope. The detailed investigation of the crystallization process indicates that two slightly different unit cells of the β-Ga structure exist during the transition. Around −50 °C the x-ray reflections of the first β-Ga unit cell (A) appear, followed at around −85 °C by additional reflections of a second cell B that co-exist with cell A. Cell A begins to vanish upon a further decrease in temperature, until below −150 °C only the reflections of cell B of the β-Ga allotrope are visible in the x-ray powder pattern. This process is reversible by subsequently re-heating the sample (cf. x-ray patterns in figure SI-22). The shortest atom-atom distances decrease from 2.64 and 2.66 Å in A...
to 2.60 and 2.62 Å in β, respectively. On the one hand this result proves that the new β′-Ga allotrope is a true phase, because the reflections we find in the x-ray pattern clearly correspond to a single phase and not to a mixture of β-Ga and γ-Ga, for example. On the other hand, these observations underline the softness of the structure and the high degree of malleability of the atom arrangement; we note that this result is also consistent with the rather flat energy versus volume curves and low energy differences calculated for these gallium allotropes (cf. section 3.9), and the high degree of atom mobility observed in the MD simulations (cf. section 3.10).

In the experiment, the cooling of the amorphous samples starting from room temperature leads to a more or less complete crystallization. An evidence for this is that the x-ray patterns of the β′-Ga allotrope are dominated by two intensive reflections at around 35° in 2θ, and show only weak further reflections up to 70° in 2θ indicating an insufficient long-range order (cf. figure 7). These two intensive reflections match with the reflections (001) and (100) of a fictive hexagonal primitive gallium structure (P 6/mmm, a = 2.84 Å, c = 2.58 Å, Ga site 1a (0,0,0)) and with the reflections (200) and (101) of the tetragonal cell of the β′-Ga structure adjusted for gallium (I4 1/amd, a = 5.20 Å, c = 2.85 Å, Ga site 4a (0,0,0)). In figure SI-23 we compare the x-ray pattern of β′-Ga to the patterns calculated for these two hypothetical structures. Both structures consist of square-like atom arrangements with similar interatomic distances but different Bravais lattice angles (see figure SI-23). The experimentally observed gallium allotropes (β′-Ga and β′-Ga) are related to these two hypothetical types.

The CASTEP/VASP calculations of the E(V) curves prove that both hypothetical structures can be plausible structure candidates for gallium as far as their energies are concerned, because these minimum energies are in the same range as those for the γ′-Ga and δ′-Ga allotropes (cf. figure SI-13d). Thus, the β′-Ga allotrope can be understood as an ‘intermediate’ during the crystallization process visible in our experiment because of the slow crystallization from the amorphous bulk. The crystallization from the solid amorphous phase involves major re-arrangements inside the relatively high-density solid, and together with the low temperature, this results in a slow crystallization dynamics. We note that the situation greatly differs from the growth from the relatively low-density deposits from the gas phase where rather fast crystallizations occur.

Structurally, the β′-Ga phase exhibits great similarities with the β-Ga, the β′-Sn and the hexagonal-primitive gallium structures (cf. figure SI-23), all of which can be derived from square-like atom arrangements, while γ′-Ga is energetically not so favorable and involves the generation of rather large nuclei (needed to accommodate the large unit cells), and the α-Ga phase is kinetically impeded as discussed earlier (see section 4.2). This is also supported by the fact that the nearest neighbor distances in amorphous Ga (about 2.9 Å, from PDF data) are more similar to those in β′-Ga and β′-Ga than to those in α-Ga [28, 29]. The advantage which β′-Ga has over the β-Ga phase is its malleability, represented by the existence of two variations that reside in the structure field spanned by the β-Ga and the hexagonal-primitive gallium structures, which allows its nuclei to form more easily inside the rather dense amorphous phase whose local structure is presumably an interpolation between the various ‘high-density’ metastable Ga-alloytropes, i.e., liquid Ga, β-Ga and the two β′-Ga variations; γ′-Ga is more unlikely as a local ‘contributor’, unless the amorphous state has been formed starting from the γ-Ga phase itself. In contrast, the direct crystallization from the amorphous lower-temperature gas phase deposits favors the β-Ga phase (and also the γ′-Ga allotrope) since the density is lower and thus pre-structures that might steer the nucleation process are less pronounced. Furthermore, the transformation of the unit cell during the calculations of the E(V) curves of the β′-Ga structure starting from the x-ray cell parameters, also reveals the high malleability of the β′-Ga structure. These results support our conclusion that the experimental β′-Ga structure can be understood as an ‘intermediate’ together with the β-Ga structure. Thus, it is possible that the final optimal structure of a gallium allotrope based on a square-like Ga-atom arrangement has not been realized up to now in the experiment.

In this context it should be mentioned that a solid solution Sn0.8Ga0.2 alloy is described which crystallizes in a primitive hexagonal unit cell (P 6/mmm) with a = 3.143 Å and c = 2.922 Å [36], analogous to the fictive hexagonal primitive gallium structure, thus supporting the structural considerations above.

### 4.4. The Ga–Sn system

The incorporation of a well-controlled specific ‘impurity’ into the gallium films is one way to gain a deeper understanding of the crystal structure formation and the corresponding phase transitions in gallium itself. For this purpose, tin is a suitable candidate, because the β-Sn structure is similar to the β-Ga structure (cf. figure SI-23) and Sn-Ga solid solutions with 4.3 wt% and 12.8 wt% of gallium have been identified and structurally characterized [35, 36]. But according to the Sn-Ga phase diagram [34], no ordered intermetallic compound of tin and gallium exists. During the deposition of gallium on tin at room temperature using the three-region method, tin clearly aided the formation of the β-Ga structure (at around –60 °C), which was the only gallium allotrope formed in addition to the β′-Sn(Ga) solid solution. The crystalline β′-Sn droplet films on the substrate surface serve as nuclei for the crystallization of the Ga atoms. Thus, because of the structural similarity to β-Sn, the β′-Ga phase crystallizes
everywhere on the substrate, while the β'-Ga allotrope does not appear. On the other hand, in the co-deposition experiments at room temperature, β-Ga and γ-Ga crystallize at −50 °C and −60 °C, respectively. We interpret this result as follows: the continuous flow of an atomic mixture of gallium and tin atoms, together with the high atom mobility on the substrate - the system is quite close to the melting point - results in a situation where only that part of the growing particles which contains tin ends up forming the β-Ga allotrope, while the remaining particles are free of tin and form the γ-Ga allotrope. This line of reasoning is supported by the β-Ga/γ-Ga ratio, which is constant across several cooling + heating cycles, and by the contrast of the corresponding EBS images, which show that only some of the particles contain tin. Furthermore, the amount of tin is much lower in the co-deposition experiments compared to the gallium deposition on tin, and all phases show a small mutual solubility which seems to influence also the crystallization process.

At lower temperatures (−190 °C) α-Ga is formed besides β-Sn, for both the three-region and the co-deposition Ga-Sn processes. This result agrees very well with the outcome of the deposition and thermal cycling of pure gallium. The only difference is the amorphization of the samples caused by the formation of the β-Sn (Ga) solid solution near room temperature. Here, the distribution of both elements on atomic level by the co-deposition experiments leads to a β-Sn(Ga) solid solution already at −190 °C with a relatively low gallium content and to an amorphization of the complete sample near room temperature.

Surprisingly, the α-Sn allotrope was never obtained during the tin deposition at substrate temperatures of 25 °C and −190 °C, including the subsequent heating + cooling cycles. In bulk systems, the phase transition between β-Sn and α-Sn occurs at 13 °C, and thus we would expect that the α-Sn allotrope should at least be formed at low temperatures. In the past, heteroepitaxial films of α-Sn have been prepared on clean InSb and CdTe (001) substrates at room temperature and have been described as a substrate-stabilized metastable phase [61]. The lack of any α-Sn phase during our experiments on sapphire substrates suggests that the influence of the substrate surface is so high that it prevents the growth of α-Sn films on sapphire substrates even at −190 °C. Thus, the depositions on InSb and CdTe mentioned above might be special and do not constitute the general case.

In this context, we note that in our calculations, we do not analyze the interface between the substrate and the Ga-films and (Ga/Sn) films. Studying the atomistic effects during the growth of the gallium films or the formation of a Ga-Sn solid solution was not in the purview of our investigation, which focuses on the (meta) stable bulk-like phases that appear in the thick films generated in the course of our experiments. The possible deformations of the unit cells of the first few Ga-layers due to the presence of the substrate may be relevant for the selection of the specific phase that grows on the substrate, but the micro-crystallites we finally observe and analyze are bulk-like.

4.5. What is the structural dilemma of elemental gallium?

The considerations in the previous subsections underline the fact that the entire discussion of elemental gallium boils down to the question: Why does gallium form so many crystal structures, and why are they so different from the usual structures found for elemental metals? To elucidate these issues, we return to the PTE. Gallium (electronic configuration [Ar]3d104 s5p) is the first element with an electron in the 4p orbital after first the 4s and then the 3d levels have been completely filled, indicating that the easy hybridization of s and p orbitals possible for elements in the second and third row of the periodic system is no longer a straightforward enterprise. We note that filling of the 3d orbitals is expected to cause a contraction of the atomic radii as function of ordinal number, due to the higher nuclear charge. Similarly, moving to higher ordinal number within a given group of the PTE is expected to lead to an increase of the atomic radii.

One way to define the (solid state) atomic radii of metal atoms is to take them to be half of the nearest neighbor atom distances in solid metals, RM [2]. Alternatively, the radii can be calculated from the overall density of the metal by the assumption of a close-packing structure (coordination number 12, valence 3), RV [62]. For the 3d-metals from scandium up to zinc, both definitions yield more or less the same value. Both radii shrink until we reach nickel and then slightly increase for copper and zinc. However, for gallium, the density based value is much larger (Ga: Rv = 1.44 Å [62]) compared to taking half the shortest atom-atom distance of the solid metal (α-Ga: Rm = 1.22 Å, β-Ga: Rm = 1.34 Å) [3]. Moreover, the atomic radii RM of the elements aluminum (Rm = 1.43 Å) and indium (Rm = 1.63 Å), which are located above and below gallium in group 13 of the PTE, respectively, are both considerably larger than the radius RM of gallium [2, 63] - a situation unique for metals in the PTE. We conclude that the close-packing used for nearly all of the metals does not seem to be a favorable arrangement of the gallium atoms. The small atomic radius of the thermodynamically stable α-Ga caused by covalent bonds forming Ga-Ga dimers hinders the formation of a closed packed arrangement, and thus RM < RV.
The structural solutions realized in gallium can be understood by considering the structures formed by the neighboring metals. Aluminum, zinc, cadmium, and indium form close packing arrangements (though tetragonally distorted for In), and germanium and tin exhibit the special tetragonal packing, respectively. Furthermore, Zn and Cd are also somewhat unusual in that the $c/a$ ratios of their hcp-based unit cells are larger than the ideal value [64] (corresponding to the increase of the atomic radius of Zn compared to Ni). The motif of the close packing is a perfect filled hexagon condensed to a layer, which is then stacked along the third dimension. However, in particular for gallium a distortion occurs resulting in the formation of a dimer via a covalent bond (involving the 4p orbitals). This causes a deformation and overall contraction of the hexagon and thus a reduced space inside of the hexagon. Therefore, the hexagons are prevented from being filled creating free volume inside the structure, and the atom arrangement realized in the $\alpha$-Ga structure consists of distorted empty hexagons in (100) layers with two short Ga-Ga distances per hexagon (see figure 20, $\alpha$-Ga in the middle). Note that all the atoms are paired up in $\alpha$-Ga, but the hexagons are formed by two parallel Ga-dimers plus two Ga atoms belonging to two different dimers (cf. figure 1). This void inside of the hexagons survives into the final $\alpha$-Ga structure, and is therefore the reason for the low density of the thermodynamic stable $\alpha$-Ga structure. To increase the density of gallium, two simple structural solutions present themselves: One approach is to employ a combination of filled 7-membered and empty 5-membered rings instead of the empty hexagons, and the other one is to form rectangles by compressing the ring along the short diagonal until a new bond forms, as seen in figure 20. Both versions are realized in the gallium allotropes, in form of the $\gamma$-Ga and $\beta$-Ga structures, respectively. We note that the rectangle motif of the $\beta$-Ga structure is similar to the tetragonal arrangement in the $\beta$-Sn structure and thus completes the structural relation to the neighboring metals of gallium in the PTE. Both allotropes, $\gamma$-Ga and $\beta$-Ga, are metastable, have a higher density but also longer Ga-Ga nearest neighbor distances (2.62/2.68) compared to the $\alpha$-Ga allotrope. The new $\beta'$-Ga structure as a distorted derivative of the $\beta$-Ga structure fits seamlessly in the structural family of $\beta$-Sn/$\beta$-Ga allotropes.

5. Conclusion

The chemical elements found in the periodic table play a fundamental role both in chemistry and in all other materials based fields of science. Clearly, their properties should be known as precisely as possible, and this knowledge should be continuously improved as new or enhanced tools become available. This applies both regarding the synthesis of their stable and metastable allotropes and for the measurements of their physical properties. Even innocent looking systems such as elemental lithium have produced many surprises in recent years, such as the appearance of the 9 R phase or the existence of phases at low temperature and ambient pressure [65, 66]. Yet the study of the structural features of the known and suspected allotropes of gallium has essentially been in hiatus for the past 30 years, although gallium - being located on the rift between the 12. and 13. groups of the PTE - exhibits many highly unusual and unexpected properties.
Employing the femtosecond pulsed laser deposition technique, we have been able to easily obtain amorphous gallium at room temperature. This is highly unusual for elementary metals: producing an amorphous state usually requires extremely high cooling rates [67]. Similarly, our generation of crystalline films has allowed us, for the first time, to measure the complete spectrum of Raman bands of \( \alpha \)-Ga, which satisfactorily agreed with the computed ones.

However, the most surprising discovery is the new \( \beta ' \)-Ga allotrope, which we could identify and characterize from the x-ray powder patterns. The existence of this new allotrope was also supported by \textit{ab initio} calculations of the equations of state of the various Ga-allotropes, which revealed nearly identical energies for \( \alpha \)-Ga, \( \beta \)-Ga and \( \beta ' \)-Ga. The high stability of the new allotrope and the thermodynamically competitive nature of these three different allotropes was experimentally supported, for example, by the simultaneous crystallization of the \( \alpha \)-Ga and \( \beta \)-Ga from the vapor phase, and by the crystallization of \( \beta ' \)-Ga from the room-temperature amorphous gallium phase during our controlled heating \(+\) cooling experiments. Crucial for this success was our experimental set-up, where we prepared the Ga films at many different well-defined conditions combined with \textit{in situ} structural and physical characterization.

Both our experiments and the molecular dynamics simulations of the various allotropes and the melt for a number of temperatures, demonstrated the complexity of the underlying energy landscape of gallium and the high degree of structural malleability of gallium even in the solid state. In particular, the detailed analysis of the x-ray powder patterns showed the presence and evolution of many kinetically stable structures in the \( \beta / \beta '/ \gamma / \) amorphous gallium superbasin on the landscape, which appears to be separated by a large free energy barrier from the \( \alpha \)-Ga region.

Of course, our study does not pretend to be the final answer on what kind of thermodynamically stable or metastable allotropes might be capable to exist in elemental gallium. In particular, long-term studies of the crystallization processes seem for us a promising tool to gain deeper insights. Nevertheless, this investigation clearly shows the importance of a periodic review of even seemingly straightforward (‘boring’) chemical systems, such as the elements themselves, opening up new vistas and yielding new insights in this process.

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