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ABSTRACT
We demonstrate the selective, pulsed-laser deposition of hexagonal GaS and monoclinic Ga\textsubscript{2}S\textsubscript{3} films on sapphire substrates from a single Ga\textsubscript{2}S\textsubscript{3} target in high-vacuum conditions. Growth at substrate temperatures below 550 °C causes GaS film formation, which indicates non-stoichiometric transfer from the target to the film. Surprisingly, stoichiometric transfer occurs at substrate temperatures above 650 °C with monoclinic Ga\textsubscript{2}S\textsubscript{3} as the preferred, higher S-content phase. Through a series of growth and annealing experiments, we show that GaS nucleation under S-deficient conditions leads to the preferred growth of this layered, hexagonal phase below 550 °C. Furthermore, GaS films annealed above 650 °C under high vacuum are transformed to Ga\textsubscript{2}S\textsubscript{3}, reflecting the greater stability of the monoclinic phase. By first growing Ga\textsubscript{2}S\textsubscript{3} at a higher temperature and subsequently growing GaS at a lower temperature, we can fabricate GaS/Ga\textsubscript{2}S\textsubscript{3} heterostructures in a single growth process.

I. INTRODUCTION
Gallium sulfide is a group III–VI semiconductor with multiple stable phases, including the (layered) hexagonal GaS phase and monoclinic Ga\textsubscript{2}S\textsubscript{3} phase. GaS has been employed in a variety of applications that require ultrathin layers, including transistors and photodetectors, and is an attractive candidate for flexible electronics.\textsuperscript{1–3} The layered GaS structure is composed of Ga–Ga and Ga–S covalent bonds that extend in two dimensions while interlayer bonding occurs via van der Waals interaction. At room temperature, the bandgap of GaS is ∼2.6 eV.\textsuperscript{4,5} Another form of gallium sulfide, the monoclinic Ga\textsubscript{2}S\textsubscript{3} phase, consists of covalent bonds in three dimensions (i.e., not layered) and has a reported bandgap of ∼3.0 eV.\textsuperscript{6–8}

Thin GaS and Ga\textsubscript{2}S\textsubscript{3} films have been grown using a variety of methods, including chemical vapor deposition (CVD), chemical vapor transport (CVT), and chemical bath deposition (CBD).\textsuperscript{3–15} Studies using these methods have demonstrated that depending on growth conditions, GaS, Ga\textsubscript{2}S\textsubscript{3}, or a combination of both phases is synthesized. More recently, one report of gallium sulfide growth was achieved by physical vapor transport (PVT) using GaS powder as the source material. GaS was found to grow at 670 °C while Ga\textsubscript{2}S\textsubscript{3} formed at 800 °C. Between these two temperatures, both phases co-existed in the film. This growth behavior was attributed to the temperature-dependent, vapor pressure difference between gallium and sulfur species.\textsuperscript{16} Other materials systems exhibiting similar III–VI and III\textsubscript{2}–VI\textsubscript{3} growth behaviors are gallium selenide\textsuperscript{17} and indium selenide.\textsuperscript{18}
II. EXPERIMENTAL

Gallium sulfide films were deposited onto c-Al$_2$O$_3$ (0001) (sapphire) substrates using the PLD technique (with a KrF excimer laser with a wavelength of 248 nm and pulse duration of 20 ns). Before deposition, each substrate underwent ultrasonic cleaning in isopropyl alcohol and oxygen plasma cleaning. Epitaxial films were obtained from a single Ga$_2$S$_3$ target. Compared to GaS, Ga$_2$S$_3$ has a higher sulfur content, which may be helpful in addressing possible sulfur deficiency in films; chalcogen deficiency can present a higher sulfur content, which may be helpful in addressing possible sulfur deficiency in films. We note that GaS species impinging on the surface should decrease with increasing temperature—a commonly observed trend in physical vapor deposition, particularly for high vapor-pressure species. We note that GaS$_2$ films as thin as 9.4 nm have been grown (see the supplementary material, Figs. S1 and S2).

III. RESULTS AND DISCUSSION

Figure 1 shows the RBS spectra of films deposited at a substrate temperature from 500 °C to 700 °C. The chemical composition and thickness of the films are presented in Table I. Below 550 °C, the Ga-to-S ratio is 1:1; from 550 °C to 650 °C, the relative amount of Ga gradually decreases (i.e., the films contain more S than Ga); and above 650 °C, the Ga-to-S ratio reaches a stable value of 2:3. In addition, the narrowing of the S and Ga signals in the RBS spectra as the substrate temperature increases shows that the films become correspondingly thinner (by over a factor of 2) despite otherwise similar growth conditions (i.e., deposition time, laser fluence, and pulse rate). This is not surprising as the sticking coefficient of vapor species impinging on the surface should decrease with increasing temperature—a commonly observed trend in physical vapor deposition, particularly for high vapor-pressure species. We note that GaS and Ga$_2$S$_3$ films as thin as 9.4 nm have been grown (see the supplementary material, Figs. S1 and S2).

Figure 2 shows the Raman spectra for films deposited at each growth temperature. For growth temperatures in the range of 500 °C–575 °C, the peaks that originated from GaS (A$_1g$, E$_1g$, and A$’$_1g) are observed. At 600 °C, peaks associated with Ga$_2$S$_3$ appear at 235 cm$^{-1}$ and 146 cm$^{-1}$ (not shown). The co-existence of peaks associated with both GaS and Ga$_2$S$_3$ indicates the presence of both gallium sulfide phases. In the temperature range in which GaS and Ga$_2$S$_3$ Raman peaks co-exist, a nominal Ga:S composition ratio between 1:1 and 2:3 is expected. We observed such a change in composition in the RBS spectra in Fig. 1 and report it in Table I. Above 650 °C, the peaks that originate from Ga$_2$S$_3$ are absent, and only peaks originating from GaS$_2$ are observed. Table I. Chemical composition and thickness at various growth temperatures determined from RBS spectra presented in atomic percent (at.%).

| Growth temperature (°C) | Ga (at. %) | S (at. %) | Thickness (nm) |
|------------------------|------------|-----------|----------------|
| 500                    | 49.5       | 50.5      | 199            |
| 525                    | 49.8       | 50.2      | 170            |
| 550                    | 49.8       | 50.2      | 158            |
| 575                    | 48.0       | 52.0      | 156            |
| 600                    | 46.0       | 54.0      | 136            |
| 625                    | 45.8       | 54.2      | 123            |
| 650                    | 40.5       | 59.5      | 83             |
| 700                    | 40.0       | 60.0      | 80             |

![Figure 1](https://home.mpcdf.mpg.de/~amal/) Raman spectroscopy using a 488 nm excitation laser and X-ray diffraction (XRD) using Cu Kα radiation provided the structural analysis. The domain size was obtained by analyzing the (002) and (111) diffraction peaks of GaS and Ga$_2$S$_3$, respectively, using the Scherrer equation.

![Figure 3](https://home.mpcdf.mpg.de/~amal/) XRD patterns of the films deposited for each sample at growth temperatures of 525 °C, 600 °C, and 650 °C. All samples display a sharp peak at 20.5° from the (0003) plane of the sapphire single-crystal substrate. GaS (002) and (004) diffraction peaks were observed at 525 °C. The (111) diffraction peak of Ga$_2$S$_3$ emerged at 600 °C. At 650 °C, the GaS$_2$ and GaS$_3$ diffraction peaks are not present, and only peaks associated with Ga$_2$S$_3$ and the sapphire substrate remain. These structural results are consistent with both Raman spectroscopy and RBS measurements and confirm the existence of three regions: at the low-temperature range (500 °C–550 °C), GaS forms; at intermediate temperatures, both GaS and Ga$_2$S$_3$ grow; and at the high-temperature range (≥650 °C),
Ga$_3$S$_2$ forms exclusively. The diffraction peaks are broader for the GaS than the Ga$_3$S$_2$ phases, indicating that the films are defective and polycrystalline with small domain sizes (<10 nm for GaS and <30 nm for Ga$_3$S$_2$) (see the supplementary material, Table S1). Nonetheless, the films are strongly textured; notably, only the (002) and (004) diffraction peaks are present for the GaS films, indicating $c$-axis (out of the plane) preferred orientation.

To understand why GaS films grow from a Ga$_3$S$_2$ target at lower temperatures, we have performed a combination of growth and annealing experiments. Table II presents the sample structures and annealing temperatures. Figure 4 shows the Raman spectrum for each sample after experiments. First, we deposited a Ga$_3$S$_2$ film, or buffer layer, at 650 °C, subsequently cooled the sample to 525 °C, and deposited a second film at that temperature. This resulted in a bilayer structure of GaS on Ga$_3$S$_2$ (on sapphire) (sample A). The GaS film is strongly $c$-axis textured (see the supplementary material, Figs. S3 and S4) displaying not only the (002) and (004) peaks of GaS but also the (006) peak. We prepared another sample by growing a Ga$_3$S$_2$ buffer layer on sapphire and cooling it to room temperature; then, we deposited another film on top of the buffer layer (sample B). In this case, the film deposited at room temperature was amorphous. Subsequently, we annealed the sample in the PLD growth chamber at 525 °C for one hour. The Raman spectrum for this sample shows evidence of only Ga$_3$S$_2$, indicating that the amorphous film transforms to Ga$_3$S$_2$ by solid-phase epitaxy (SPE).

This behavior is consistent with the theory of intrinsic SPE, whereby the buffer layer seeds solid-phase homoepitaxy with no barrier to nucleation. In the absence of a Ga$_3$S$_2$ buffer layer, an amorphous film deposited directly on sapphire and annealed at 525 °C crystallizes predominantly in the layered GaS phase (sample C); the Raman spectrum contains a strong peak from GaS and a small signal that may be attributed to the Ga$_3$S$_2$ phase. This suggests that the enhancement of S locally in the solid phase (amorphous film) enables nucleation of some Ga$_3$S$_2$ even as most of the film crystalizes as GaS. We note that the amorphous films have a Ga: S atomic composition near 1:1 despite the use of a Ga$_3$S$_2$ target.

A fourth sample (D) was prepared by first depositing a GaS film on sapphire at 525 °C followed by an amorphous film at room temperature. The sample was then annealed at 650 °C. Following annealing, the Raman spectrum shows evidence of only Ga$_3$S$_2$, demonstrating that this is the more stable phase at elevated temperature under high-vacuum conditions—specifically, the GaS buffer layer underwent a solid-phase transformation to Ga$_3$S$_2$.

The successful SPE of Ga$_3$S$_2$ from a Ga$_3$S$_2$ buffer layer suggests that conditions could exist that will lower the temperature for Ga$_3$S$_2$ nucleation and growth; that is, experimental parameters in PLD may exist to drive a preference for the formation of Ga$_3$S$_2$ over GaS.

**TABLE II.** Pulse-laser-deposited films and annealing temperature.

| Sample | Synthesized film structure | Annealing temperature | Film phase(s) after annealing |
|--------|----------------------------|-----------------------|-----------------------------|
| A      | GaS(epi)/Ga$_3$S$_2$(epi)/sapphire | N/A                   | N/A                         |
| B      | Amorphous Ga–S/Ga$_3$S$_2$(epi)/sapphire | 525 °C | Ga$_3$S$_2$ |
| C      | Amorphous Ga–S/sapphire | 525 °C | GaS (major) Ga$_3$S$_2$ (minor) |
| D      | Amorphous Ga–S/GaS(epi)/sapphire | 650 °C | Ga$_3$S$_2$ |

**FIG. 2.** Raman spectra of synthesized films at different growth temperatures—from top to bottom, 500 °C, 525 °C, 550 °C, 575 °C, 600 °C, 625 °C, 650 °C, and 700 °C. The spectra of the films transition from showing peaks from only GaS at low temperature, to peaks from a mixture of GaS and Ga$_3$S$_2$ at intermediate temperatures, to peaks from only Ga$_3$S$_2$ at elevated temperatures.

**FIG. 3.** X-ray diffraction patterns for films deposited on sapphire at different deposition temperatures. The film deposited at 650 °C is single-phase, monoclinic Ga$_3$S$_2$. At 625 °C and 600 °C, the films consist of a phase mixture, monoclinic Ga$_3$S$_2$ and hexagonal GaS. The film deposited at 525 °C shows peaks associated with GaS.
GaS at lower temperatures. In physical vapor deposition processes, this might be accomplished by either modifying deposition fluxes or changing the substrate. To test this hypothesis, we substituted sapphire substrates with Si substrates in three different orientations—Si (111), Si (110), and Si (100)—and deposited films under the PLD conditions described previously. The measured Raman spectra are presented in Fig. S5 and used to identify the phase(s) present in the film as done previously. Table S2 summarizes our findings, which show that indeed, GaS3 can grow at lower temperatures on Si than sapphire. Therefore, we see that both substrate material and crystal orientation provide control over phase nucleation across temperature.

The standard Gibbs free energy of formation of GaS3 is lower than GaS over the growth-temperature range (500 °C–700 °C). However, under our growth conditions—namely, high vacuum—GaS is the preferred thin-film phase at low temperature. Growth under S-deficient conditions favors the nucleation of GaS over GaS3. At higher temperatures, GaS3 nucleation is preferred even under S-deficient conditions, and GaS no longer grows. The nucleation behavior can be controlled by the substrate material and orientation, pushing GaS3 growth to lower temperature. The amorphous and GaS films transform to GaS3 upon annealing at 650 °C, demonstrating the greater stability of GaS3 at higher temperature under the experimental conditions used; using a sapphire substrate, we were not able to grow a GaS3 film at 650 °C on a previously grown GaS film as the GaS film undergoes a solid-phase transformation to GaS3 at this temperature.

**IV. CONCLUSION**

In summary, pulsed-laser deposition under high vacuum conditions can be used to grow GaS and GaS3 films from a single GaS target. While stoichiometric transfer occurs at temperatures above 650 °C, the lower-sulfur-content GaS phase is preferred below 550 °C. By changing the substrate temperature within a narrow range, heterostructures of hexagonal (layered) GaS and monoclinic (non-layered) GaS3 can be synthesized from a single process, providing unprecedented opportunities to realize heterojunctions from a single materials system and investigate the heteroepitaxy of van der Waals semiconductors on three-dimensional, covalently bonded semiconductors.

**SUPPLEMENTARY MATERIAL**

See the supplementary material for the RBS and Raman spectra of a sub-10-nm-thick GaS film are presented. In addition, the calculated crystalline domain sizes of GaS and GaS3—obtained from analysis of XRD peaks—are presented. Finally, the Raman spectra and phase information of gallium sulfide films grown on silicon substrates are reported.

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**DATA AVAILABILITY**

The data that support the findings of this study are available within the article and its supplementary material.

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