Chemically driven growth of Au-rich nanostructures on AIII-BV semiconductor surfaces

B.R. Jany*, A. Janas*, W. Piskorz*, K. Szajna*, A. Kryshtalb, G. Cempurac, P. Indykac, A. Krukb, A. Czyrska-Filemonowiczb, F. Kroka

*Marian Smoluchowski Institute of Physics Jagiellonian University, Lojasiewicza 11, 30-348 Krakow, Poland
bInternational Centre of Electron Microscopy for Materials Science, AGH University of Science and Technology, 30-059 Krakow, Poland
cFaculty of Chemistry, Jagiellonian University, ul. Gronostajowa 2, PL 30-387 Krakow, Poland

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Abstract

The AIII-BV semiconductors, due to their unique properties, are considered for decades as a promising material to overcome the limitations of the silicone semiconductor electronic devices. One of the important aspects in the AIII-BV semiconductor technology is gold-semiconductor interactions at the nanoscale, since gold is widely used to catalyze the growth of AIII-BV structures and it is also an important material for the electronic device mainly used as electrodes. Here, we report, by investigation of the nanostructures formed in the process of thermally induced Au self-assembly on various AIII-BV semiconductor surfaces (InSb(001), InAs(001), InP(001), GaSb(001), GaAs(001), GaP(001)), how Au interacts with each material at atomic scale as provided by

* Corresponding author e-mail: benedykt.jany@uj.edu.pl
the atomically resolved aberration corrected HAADF STEM measurements. The Au diffusion into bulk AIII-BV crystal lattice was seen only for InSb crystal, and investigated at atomic level experimentally by Machine Learning HAADF image quantification and theoretically by detailed Density Functional Theory (DFT) calculations. Our studies uncovered also that independently of the interaction between Au and AIII-BV semiconductors the formation of the nanostructures is driven by the surface diffusion and nucleation of adatoms, produced by Au induced chemical reactions of AIII-BV bounds breaking on the semiconductor surfaces. We show that the type of the Au-rich phase, which forms the developed nanostructures, depends on the AIII-BV semiconductor binding energy. From the reaction stoichiometry we were able to estimate the number of AIII-BV bounds broken due to the interaction of single Au atoms on the surface. It has been found also a difference in the Au interaction between In- and Ga-based AIII-BV semiconductors as confirmed by Machine Learning methods. Our comprehensive systematic studies uncover the details of Au on AIII-BV surface interaction at the atomic level with chemical sensitivity.

Introduction

AIII-BV semiconductors due to their unique properties such as high electron mobility and direct bandgap are considered as a material for new generation of nanoscale electronic devices [1-3]. Recently, new technologies were developed like template-assisted selective epitaxy (TASE) by IBM Zurich group [4] and epitaxial lift off (ELO) technique by Korean group [5] to integrate AIII-BV with Si at nanoscale. This will allow expanding the use of AIII-BV crystals by extending the conventional Si-based technology for future AIII-BV/Si nanodevices fabrication [6]. For many applications array of standing, vertically aligned AIII-BV nanowires grown on semiconductor surfaces are desired [7-9]. It has been shown that such AIII-BV nanowires can be used to water splitting in a very efficient way [10]. Also AIII-BV nanowire LED device integrated on Si was developed, having 3 orders of magnitude higher efficiency than the conventional device [11]. For controlling the physico-chemical properties of the devices the local information of atomic arrangement is necessary as recently shown by atomic resolution spectrum imaging in STEM [12]. The growth of this monocrystalline AIII-BV nanowires is mainly catalyzed by Au seeded nanoparticles [13]. Studies on the role of Au in the process of nanowires growth, in the closed system being in equilibrium, have been performed by Dick et al. [14].
They showed that Au is not inert with respect to AIII-BV semiconductor material and it interacts with the substrate forming a variety of intermetallic compounds (alloys) in the Au-AIII system. In this respect the process of thermally controlled self-assembling of Au thin layer on reconstructed AIII-BV surfaces in UHV conditions is a method of choice to create patterns of well-ordered nanostructures. Au interactions with AIII-BV semiconductors and development of new phases is governed by the relations of Au-In-BV and Au-Ga-BV ternary phase diagrams [15-17] (see also supporting information Fig. S2). These ternary phase diagrams show that there are varieties of stable phases in the Au-AIII systems (see also Table S2) and only two stable phases for Au-BV pairs i.e. AuSb$_2$ and Au$_2$P$_3$. Thus, the Au interactions with whole group of AIII-BV is dominated by the Au-AIII phases formation as defined by the Au-In and Au-Ga binary phase diagrams [18; 19]. The above rules hold also in the present case of “an open system”, where BV element is volatile and escapes to the vacuum while annealing the samples [20; 21].

We have investigated the thermally induced self-assembly of 2 Mono-Layers (ML) of Au with various AIII-BV (001) semiconductor crystal surfaces in ultra-high vacuum (UHV) conditions. By means of various electron microscopy-based techniques the Au/AIII-BV interaction at atomic scale with chemical sensitivity has been investigated. We have found that there is a large difference between the Au interactions for In- and Ga-based substrates. Our investigations prove that the Au content in the nanostructures formed depends on the binding energy between AIII-BV components. The formed nanostructures could be later used as a seeds for the nanowires growth, substituting Au seeding by nanoparticles [22]. Recently it has been shown that thermally activated motion of Au droplets on the AIII-BV crystal surfaces can lead to new asymmetric morphologies for use in nanophotonic devices applications [23]. The formed metallic phase at nanostructure influences also the electronic properties of metal-semiconductor nanodevice due to the appearance of the Schottky barrier (the Schottky contact is formed). When the barrier value approaches to zero, ohmic contacts are formed [24; 25]. The electronic properties of the interfaces formed has impact on the development of future nanoelectronic devices based on AIII-BV technology [26], like nano Schottky diodes [27; 28].

Results

_In-based AIII-BV semiconductor substrates - InSb(001), InAs(001) and InP(001)_

Figure 1: Nanowires on InSb(001) surface formed after deposition of 2ML Au at 330 °C. a) RHEED pattern of the clean and reconstructed c(8x2) InSb(001) surface, b) SEM and c) AFM images of the morphologies of the nanowires, d) Nanowires length distribution, e) Atomically resolved HAADF STEM image of the nanowire cross section, Au diffusion into the bulk (marked area B) is clearly seen. At the low corner the InSb crystallographic directions are indicated, f-h) corresponding EDX chemical maps of Au, Sb and In, respectively, i) EDX line profile through the nanowire/substrate interface, j) atomically resolved HAADF image of the InSb substrate, k) Au concentration map within the atomic InSb columns – the Machine Learning HAADF STEM quantification of the area B (Au diffusion region), different amount of Au builds up into InSb lattice (value “1” corresponds to the concentration of 100 at. %), l) Detailed view on the interface between AuIn2(001) nanowire and InSb(001) with proposed atomistic structural model of the interface overlaid in the HAADF image.

The deposition of 2ML of Au on a clean c(8x2) reconstructed surface of InSb(001) monocrystal at 330°C results in the formation of long nanowires oriented along [-110] substrate surface direction as depicted in Fig. 1b). The nanowires have a length of ~500 nm and width of ~70 nm, what corresponds to the average square equivalent size of 143+/−11 nm, as derived from Scanning Electron Microscopy.
The nanowires have a constant height of ~5 nm, as indicated by Atomic Force Microscopy (AFM) measurements (Fig.1c and d).

In Fig. 1e the atomically resolved High Angle Annular Dark Field (HAADF) Scanning Transmission Electron Microscopy (STEM) image of the nanowire’s cross section is presented. In HAADF STEM the imaging contrast is proportional to the atomic number Z and thus this technique ensures the chemical sensitivity (the Au atomic columns appear brighter than In-Sb columns). Due to a very high sensitivity of this technique, small variations in the composition for AIII-BV alloys could be detected [29]. It is seen that the nanowire is crystalline and is composed of Au and In without Sb as indicated by EDX measurements (Fig.1f-i). This points out that during the process of nanowire growth, the Au interactions with substrate InSb surface result in breaking bonds between In and Sb atoms. A stable Au-In phase is formed (see supporting information Fig. S2a and Table S2) while Sb atoms escape from the sample to the vacuum. By examining the interplanar spacing of the atomic columns and their contrast in the HAADF STEM imaging, the nanowire composition is identified as AuIn$_2$ alloy phase [19]. AuIn$_2$ nanowire’s stoichiometry is confirmed also by SEM/EDX measurement results which were analyzed by a newly developed method of chemical quantification based on Machine Learning approach [30]. The driving process of chemical reaction under consideration on the sample surface is

$$\text{Au} + 2\text{InSb} \rightarrow \text{AuIn}_2 + 2\text{Sb} \uparrow | \Delta H = -0.215 \text{eV} |$$

[31; 32]. One can conclude that for these experimental conditions one Au atom breaks two In-Sb bounds on the InSb (001) substrate surface. Fig. 1e depicts that AuIn$_2$ nanowires grow epitaxially on the InSb substrate with the epitaxial relationship of (001)AuIn$_2$///(001)InSb and [110]AuIn$_2$/|[110]InSb. Such epitaxial relations of the system were also predicted by the computational model [32; 33]. The nanowire is partially buried below the average substrate surface level and is surrounded on its sides by crystalline rim having common (111) facet plane. The AuIn$_2$ nanowire exposes on its top the (001) plane of square-symmetry in agreement with previous atomically resolved imaging with non-contact atomic force microscopy [34]. From Fig. 1e it is also clearly seen that the HAADF STEM contrast of the InSb substrate crystal is not uniform. The region just below the nanowire (marked as region B) is brighter than the rest of the InSb bulk (region A) indicating that the region B is enriched in Au due to the diffusion (dissolution) of Au atoms into the InSb crystal. The corresponding EDX measurements (Fig. 1f-i) exhibit the enrichment in Au and deficit in Sb of the region B. To distinguish between pure In-Sb columns and these containing Au atoms (assuming constant sample thickness) the HAADF image quantification was performed. Due to the noise inherent to the experiment, intermixing between the Au and In-Sb phases is studied statistically.
using Machine Learning algorithms as implemented in Trainable Weka Segmentation [35] (for details see supporting information Fig. S1 and Table S1 and the method section). The results of Machine Learning HAADF image quantification of the Au enriched region is presented in Fig. 1k, as an Au atomic concentration map. The Au does not uniformly populate the In-Sb lattice atomic positions (see supporting information Fig. S2d, Table S1). The formation of AuIn$_2$ phase after Au layer annealing on InSb(111) was previously observed by HRTEM [36] but without a chemical sensitivity at the atomic level so the Au diffusion was not studied. In Fig. 1l atomically resolved HAADF STEM image of the interface between AuIn$_2$ (001) and InSb (001) is presented. The epitaxial relations of the interface are clearly demonstrated by the continuation of the atomic rows between the AuIn$_2$ nanowire and InSb substrate. The proposed structural model of the interface is overlaid on the atomically resolved HAADF STEM image (Fig. 1l).

The observed Au diffusion into InSb lattice was still investigated in detail and the results are shown in Fig. 2. Fig. 2a shows atomically resolved HAADF STEM of one In-Sb dumbel, for better visibility of Z contrast the false colouring was used. One can clearly distinguish between A(In) and B(Sb) atomic columns. The Au atomic concentration maps in: antimony atomic sub-lattice A(Sb) (see Fig. 2b) and indium atomic sub-lattice B(In), (see Fig. 2c) was extracted from the results of the atomic HAADF image quantification. It has been found that the antimony sub-lattice is more populated with Au (on average ~18 at. % of Au) than the indium atomic sub-lattice (on average ~13 at. % of Au). It is also seen that the Au concentration in both sub-lattices decreases when the distance from the island increases. To characterize the difference in Au incorporation into different atomic sub-lattices the ratio map of atomic concentration was constructed defined as $R=[Au \text{ in } A(Sb)]/[Au \text{ in } B(In)]$ and shown in Fig. 2d). In Fig. 2e) the plot of the experimental R value against the average Au concentration is presented. Depending of the average Au concentration regions with a high R and low R (~1) values are observed. Thus, for the low Au concentration, Sb lattice is much more populated with Au than In lattice while for the high Au concentrations both sublattices are equally populated with Au.

To describe the process of Au atoms incorporation into InSb lattice we employed state of the art first principles DFT calculations with addition of the temperature via the harmonic vibrational analysis ($T=330 \, ^{\circ}\text{C}$) giving the vibrational entropy contribution to the Gibbs free energy and the results are shown in Fig. 2e)-f).
Figure 2: Au diffusion into InSb substrate resulted from the deposition of 2ML Au at 330 °C. a) false colouring atomically resolved HAADF STEM, antimony A(Sb) and indium B(In) lattice is marked. Results of HAADF image quantification, experimental Au concentration map in b) antimony lattice A(Sb), c) indium lattice B(In), d) Au concentration ratio $R=[\text{Au in A(Sb)}/[\text{Au in B(In)}]$ map. The Au concentration decreases as the distance from the nanowire increases. Experimental Au concentration ratio $R$ as a function of the average Au concentration (value 1 corresponds to 100 at. %) e), two regions are clearly visible I and II, for the small Au concentrations (below ~13 at. %) the Au preferentially builds up into the antimony A(Sb) lattice ($R>>1$). As the Au concentration increases (~25 at. % and above), the population in Au of both lattices gets equal ($R\sim1$) (the line is drawn to guide the eye). Results of DFT calculations at $T=330^\circ\text{C}$ via vibrational analysis showing stable Au/InSb structures for different regions of Au concentration f).
Fig. 2e) shows the experimental concentration ratio $R$ together with the $R$ values resulted from DFT results are shown in terms of energetically preferable $R$ value versus average Au concentration. Here, as in the experiment, also two regions are visible: Region I, for the average Au concentrations less than ~13 at. %, where the high $R$ values are energetically preferable accordingly to the Gibbs free energies and Region II, for average Au concentration higher then ~25 at. %, with $R$ values ~1. A good agreement between the experimental and calculated $R$ has been found. Between these two regions a Transitional Region with undefined $R$ values as provided by the DFT calculations is defined. The DFT calculations define additionally energetically preferable Au/InSb structures for observed two regions (see in Fig. 2f). For the case of Region II, i.e., $R$ values close to “1” the Au atoms incorporated into the In/Sb columns agglomerate leading to formation of Au dimers/oligomers as most energetically preferable configurations (having smallest Gibbs free energies). Thus, formation of Au atomic wire-like structures in InSb lattice is predicted. Next, two contradictory effects results from DFT simulations: the lattice swelling due to the introduction of Au atoms (longer atomic radii) and, when Au-dimers are

Figure 3: Au diffusion into InSb substrate resulted from deposition of 2ML Au at 330°C. a) Experimental results of Geometric Phase Analysis (GPA), different strain components are presented. Below the nanowire (area of ~2nm) dominant positive ~3% $\varepsilon_{yy}$ strain field is visible. No correlation is observed between the GPA lattice strain and the amount of Au diffusion. No GPA strain is visible in the Au diffusion area (area of ~10nm below the nanowire). Au concentration maps for antimony b) and indium c) sublattices and corresponding atomic columns ellipticity maps for antimony d) and indium e). Vector Field Plots of antimony f) and indium g) atomic columns ellipticity. The vector line length is proportional to the ellipticity values. InSb crystallographic directions indicated.
formed, the shortening of the Au-Au bonds. When the equilibrium Au doping takes place, the dimers/oligomers are preferentially formed and thus no significant lattice swelling is observed.

The lattice strain obtained by Geometric Phase Analysis (GPA) of atomically resolved HAADF STEM images, which traces the local deformation of atomic lattice unit cell in the x-y plane perpendicular to the electron beam (z direction) is presented in Fig. 3a. Just below the nanowire, in the region of around 2nm, a dominant positive ~3% of $\varepsilon_{yy}$ growth strain field is visible, meaning ~3% expansion of the atomic lattice in y direction (growth direction). Any correlation between the observed strain fields and the amount of Au atoms incorporation into InSb lattice has not been found. According to experimental data, the region where the Au diffusion takes place (area of ~10 nm below the wire) is strain free. This observation is consistent with DFT simulation predictions. The strain filed is only visible in the region of ~2 nm below the nanowire.

To elucidate in details the atoms off-axis positioning within the atomic columns in the Au diffusion area, we performed atomic columns shape analysis via ellipticity analysis of the HAADF STEM images [37; 38]. Each atomic columns was fitted with an elliptical 2-D Gaussian. The ellipticity parameter was extracted and defined as the ratio of long to short ellipse axis accordingly to Nord et al. [38]. The ellipticity value of “1” corresponds to perfectly circular atomic columns while values greater than “1” indicates changes of atom positions, within atomic columns parallel to the beam direction (z), in the x-y plane [37; 38]. The ellipticity maps are plotted for the part of Au diffusion area, as indicated in Fig. 2b-c), and are presented separately for Sb and In atomic columns. Fig. 3b-c) shows Gold (Au) concentrations maps and corresponding ellipticity maps Fig. 3d-e). It is seen that high ellipticity value corresponds to the regions of low indium concentration in the atomic columns, i.e., of high R values region. In the regions where Indium and Antimony lattices are both highly populated with Au (low R values region ~1) the ellipticity is close to “1”, i.e., there is no atomic position changes within the column. In Fig. 3f-g) the ellipticity is plotted, for indium and for antimony atomic rows respectively, as a vector field plot where the length of a vector line is proportional to the ellipticity value. Additionally to the magnitude also the ellipticity direction could be visualize so the direction of the atomic position changes within the column is seen. The Au concentration in the InSb crystal sublattices highly influences the ellipticity of the atomic columns and its direction. For example in following we describe three regions marked as (1), (2), (3) in Fig. 3b-g):
(1) for the case of Au concentration in In of ~11 at. % and in Sb of ~18 at. % sublattice (R value ~1.6), the ellipticity values are for Indium (~1.4) and Antimony (~1.2) atomic columns, respectively. The ellipticity direction is the same for In and Sb case i.e. the atomic displacement within the column are happening in the InSb [111] direction for both Indium and Antimony atomic columns.

(2) for the case of Au concentration in In of ~5 at. % and in Sb of ~11 at. % sublattice (R value ~2.2), the ellipticity values are comparable (~1.2) and the ellipticity direction is the same for In and Sb sublattice.

(3) for the case of Au concentration in Sb of ~5 at. % and no diffusion into In sublattice (very high R value), the ellipticity for Sb is high (~1.4) and is directed along [110] InSb direction, while the ellipticity for In is smaller (~1.1) and is directed along [111] InSb direction.

In Fig. 4 a)-b) morphologies of surface nanostructures resulted from the deposition of 2 ML of Au on InAs(001) and InP(001) at 330 °C are shown, as seen by SEM and AFM, respectively. In both cases, the nanostructures are less anisotropic than for ones formed for the Au/InSb(001) system. In the case of Au/InAs(001) the nanostructures, slightly elongated along [-110] direction, have an average size of ~36 nm whereas for Au/InP(001) round nanostructures with the sizes of ~31 nm are formed. The atomically resolved HAADF images (Fig. 4) show that for both cases the nanostructures are in registry with the substrates. It has been found that for the case of Au/InAs(001) system the developed nanostructures are composed of alloy of the Au$_3$In phase (Fig. 4 c)-d)) with the epitaxial relationship (001)Au$_3$In//(001)InAs and [100]Au$_3$In//[110]InAs. We identify the driving process of the chemical reaction as follows

$$3 \text{ Au} + \text{ InAs} \rightarrow \text{ InAu}_3 + \text{ As} \uparrow \Delta H = -0.007 \text{ eV}$$

[31; 32]. In this case the nanostructures grow above the average substrate surface level as indicated in Fig. 4c). This is related to the kinetics of growth process where Au atoms break the bond of InAs substrate dimers and nucleate with the released In atoms to form finally clusters (islands) of In/Au alloy (As atoms evaporate to vacuum). The islands form a kind of mask, which blocks further InAs bound breaking underneath. Thus, further incoming Au atoms can break only InAs bound, which are outside of the mask region inducing the lowering of the substrate surface level outside of the appearing AuIn nanostructures. The detailed view on the interface with atomistic structural model of the phases is presented in Fig. 4d). In turn, for the Au/InP(001) system the nanostructures formed are of AuIn$_2$ phase (see Fig. 4e)-f)) with the
epitaxial relationship (-11-1)AuIn\textsubscript{2}/(001)InP and [110]AuIn\textsubscript{2}/(110)InP. This defines the chemical reaction as \( Au + 2 \text{InP} \rightarrow Au\text{In}_2 + 2 \text{P} \uparrow | \Delta H = 0.172 \text{eV} \) [31; 32]. The formed nanostructures extend slightly below the average substrate level as depicted in Fig. 4e). For both substrates, InAs and InP, we see dominant coherent interface, which defines the nanostructures growth. No additional faceting or Au diffusion into the substrate bulk is observed, as it was the case for Au/InSb(001). The process of Au interaction with InP leading finally to an AuIn alloy formation was recently extensive studied for the Au catalyzed InP nanorods growth [39]. It was found that stoichiometry of the In-Au alloy phase depends on the diameter of nanowires, which was explained by the In supersaturation in the Au nanoparticle and limited diffusion due to the finite size of nanowires. In our case we do not see any nanostructure size dependent effects, since the diffusion is not limited and we have almost infinite InP surface.

Figure 4: Nanostructures resulted from the deposition of 2ML of Au at 330°C on: InAs(001) a) SEM image, c)-d) atomically resolved HAADF STEM images and on InP(001) b) SEM, e)-f) atomically resolved HAADF STEM images. Detailed view on Au\textsubscript{3}In/InAs interface d). Detailed view on the nanostructure e) and bulk f) for the case of InP. Substrate crystallographic directions are marked. All nanostructures are in epitaxy with the AIII-BV substrates.
Ga-based AIIIBV semiconductors GaSb(001), GaAs(001) and GaP(001)

The clusters/nanoislands formed after deposition of 2ML of Au on the reconstructed c(3x1) GaSb(001) surface at 330 °C are examined by SEM/AFM and the results are shown in Fig. 5a). The nanostructures have an average lateral size of ~13nm and a constant height of ~3nm. In contrast to the Au/InSb, here no shape anisotropy of the nanostructures is seen. To uncover the detailed internal nanostructures’

Figure 5: Nanostructures resulted from deposition of 2ML of Au at 330 °C on GaSb(001) a) SEM image morphology, d)-f) atomically resolved HAADF STEM images, on GaAs(001) b) SEM image, g) atomically resolved HAADF STEM image and on GaP(001) c) SEM image, h) atomically resolved HAADF STEM image. Substrate crystallographic directions marked. All formed nanostructures are in epitaxy with the AIII-BV substrate.

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structure the TEM measurements were performed and the atomically resolved HAADF STEM image of the nanostructure’s cross section is presented in Fig. 5d)-f). By examining the interplanar spacing of the atomic columns together with the results of the EDX experiments and HAADF contrast, the nanostructure phase is identified as an AuGa\textsubscript{2} alloy phase (see Fig. 5e). No indications of Sb incorporation in the nanostructures formed have been found. Thus, the Au interactions with GaSb at elevated temperatures lead to formation of one of the stable Au-Ga phase (see supporting information Fig. S2d and Table S2) and releasing of Sb atoms into vacuum. The process driving chemical reaction on the sample surface in this case would be $Au + 2GaSb \rightarrow AuGa\textsubscript{2} + 2Sb \uparrow \left( \Delta H = -0.046 \text{ eV} \right)$.[31; 32].

One sees that the AuGa\textsubscript{2} nanostructure grows by forming preferentially (111) crystallographic facets which are in registry with (111) GaSb facets. We have also found that there is no Au dissolution in GaSb bulk in close vicinity of the nanostructure grown. The formed AuGa\textsubscript{2} nanostructures are in epitaxy with GaSb(001) with the following epitaxial relationship: (001)AuGa\textsubscript{2}//(001)GaSb and [110]AuGa\textsubscript{2}//[110]GaSb. Such relationship was already predicted based on the computational model [32; 33].

In the case of Au/GaP(001) system, the nanostructures with an average lateral size of ~6nm i.e. two times smaller than in the case of Au/GaSb are formed (see Fig. 5c). In Fig. 5h) the atomically resolved HAADF STEM image of the nanostructure cross section is shown. The analysis of interplanar spacing of the atomic columns indicates that the nanostructures formed are of pure Au phase. The process driving chemical reaction on the sample surface in this case is $5.9 Au + GaP \rightarrow 5.9 Au + Ga + P \uparrow \left( \Delta H = 0.823 \text{ eV} \right)$[31; 32]. In this reaction, the amount of Au atoms involved in the process is estimated, as a fraction of the nanostructure cross-section area which is below the sample average surface level as taken from HAADF image. One can assume that only this part of GaP underwent reaction with Au. Otherwise, in the absence of reaction with Au the formed nanostructures would be fully on the sample surface. The Au interaction with GaP resulting in the formation of AuGa alloy was earlier observed for the case of Au catalysed-nanorods growth with the Au seeds (particles) size less than 15nm. For these Au seeds dimensions the nanoparticle size dependent effects were observed [14]. In the present case any size-depend alloying effects are observed, since the Au diffusion is unlimited on the GaP crystal surface. The interfaces between the Au nanostructure and the substrate is of the following epitaxial relationship (001)Au//(001)GaP and [110]Au//[110]GaP in agreement with the computational model predictions [32; 33].
For the third Ga-based substrate material studied, i.e., GaAs(001) the thermally induced self-assembly of 2 ML of Au leads to development of small, 8.2 nm clusters uniformly distributed on the substrate surface (Fig. 5b). The HAADF and EDX measurements provide that the clusters are of pure Au phase. They grow with their (001) planes in epitaxy with (001) GaAs substrate surface planes and side walls of (111) facets. The epitaxial relationship in this case is also (001)Au//(001)GaAs and [110]Au//[110]GaAs in agreement with previous studies [40]. The formed Au structures are partially submerged into the GaAs substrate similarly to the case of GaP(001). The process driving chemical reaction is
\[ 2.5 \text{Au} + \text{GaAs} \rightarrow 2.5 \text{Au} + \text{Ga} + \text{As} \uparrow | \Delta H = 0.701 \text{eV} | \] [31; 32]. Here the same as in GaP case, the amount of Au atoms involved in the process is estimated, as a fraction of the nanostructure area which is below the sample average surface level, to the area of whole Au nanostructure, as from HAADF image. Recently the Au interactions with GaAs(111) nanowires at elevated temperatures was studied in situ by TEM experiments [41]. It was found that the Au replacement proceed by one GaAs(111) bilayer at a time and no fixed epitaxial relation have been found. Only after the cooling of the sample the formed Au-rich phase was identified as AuGa intermetallic. This can be explained in terms of limited Au diffusion in the nanorods width and finite amount of GaAs available for the system in opposite to the present case with the unlimited diffusion and almost infinite amount of GaAs available for the system as compared to the 2 ML of Au.
Discussion

The set of seven experimental parameters of the studied nanostructures extracted from the SEM, AFM and TEM measurements like size, height, Au content, etc. (see Table S3 in supporting information), were analyzed by Machine Learning methods to extract the existing relations between them. Instead of looking at the parameters one by one or in groups by two, which will integrate the data over other

Figure 6: Nanostructures resulted from 2ML Au deposited on InSb(001), GaSb(001), GaAs(001), InP(001) and InAs(001) surfaces at 330°C. a) Machine Learning Multidimensional Scaling (MDS) 2D projection of measured nanostructure parameter’s space. Result of k-means clustering indicated as red and blue color. b) structure average lateral size versus average surface diffusion radius, together with linear fit to the data. c)-d) Nanostructure-AIIBV semiconductor interface type for Indium and Gallium based semiconductors, crystallographic AIIBV planes together with their relative occurrence are given.
dimensions, one can employ the multidimensional scaling (MDS) [42] to visualize these seven dimensions “simultaneously” on the plot, without any assumption on ordering. The MDS is a technique which finds low dimensional projection (two dimensional) of the multidimensional data on the plane by trying to preserve the distance between the points as good as possible. So the points with similar properties in multidimensional space are closer together in MDS projection. We used here also for this seven dimensional data clustering algorithm which works in multidimensional parameter space, i.e., k-means clustering method [43], which searches for the group of points which are close together (clusters). In Figure 6a) computed MDS projection of the map into 2D plot together with the results of k-means clustering is presented. The k-means clustering found two clusters in the data, which are nicely seen on the MDS map, one cluster for indium- and one for gallium-rich AIII-BV substrates. This shows that taking only parameters of the formed nanostructures, without assuming any explicit ordering, one sees two groups of different behaviour for indium-rich and one for gallium-rich AIII-BV semiconductors. This shows that Ga-rich and In-rich AIII-BV semiconductors interact completely differently with Au. This is related to different AIII-BV compound stability when contact with gold [14]. Furthermore, the morphological parameters, i.e., average size, surface density, and average surface diffusion radius, of the nanostructures grown on the In-rich and Ga-rich substrates split into separate groups when they are studied as a function the heat of formation (binding energy) - HoF of the AIII-BV semiconductor [44], which is used here as an explicit ordering parameter, where the most negative value corresponds to the highly bound system Fig. S4 (see supporting information).

There is also a strong linear correlation between the structure average size and average surface diffusion radius for all studied AIII-BV substrates as depicted in Fig. 6b). This indicates that independently of the chemical interaction mechanism of Au and AIII-BV semiconductor the nanostructures formed are mainly a consequence of the surface diffusion of adatoms and their nucleation.

In Fig. 6 c)-d) the interface composition of the nanostructure/AIII-BV semiconductors is presented for indium and for gallium rich semiconductors, respectively. The AIII-BV facets formed at the interfaces are plotted as a function of the heat of formation for AIII-BV semiconductor. The relative occurrence, in percent, of particular facets is given and the facets are ordered accordingly to their stability, i.e., surface energy [45]. It is seen that for the InSb, the semiconductor with the lowest binding energy, there is high Au-induced etching of (001) surface and facets with higher stability are formed (311) and (111) Fig. 6c). As the semiconductor binding energy increases (InAs and InP) it is very difficult to etch (001)
surface for the same conditions, thus only (001) facets are present. The situation looks the same for
gallium based semiconductors as shown in Fig. 6d). For the lowest binding energy (GaSb) the (001)
surface etching is very high, so only (111) facets are formed. When the binding energy increases
(GaAs) the (001) facets start to appear (40%) and for the still increasing of binding energy (like GaP)
the (001) facets start to dominate (70%). As in the case of AIII-BV compound semiconductors, the
hierarchy in surface etching by Au atoms and facets formation is observed for simple single-component
semiconductors such as Si or Ge [46; 47].

The mechanism of metal etching seems to the main process of the nanostructure interface formation
due to preferential etching of surface and leading finally to formation of the stable facets, i.e., facets
having the smallest surface energies [45]. Later, the Au/Au-AIII metal nanostructures grow by forming
preferentially (111) crystallographic facets, since the facets have lower surface energy [48; 49].

In Table 1 an experimentally evaluated number of Au atoms engaged into break one AIII-BV bound
together with a leading chemical reaction and heat of formation of AIII-BV semiconductor is presented.

| Examined System | AIII-BV Heat of Formation [kJ*mol⁻¹] | Chemical Reaction (ΔH - calculated reaction enthalpy [31] [32]) | Number of Au atoms needed to break one AIII-BV bound on surface (this experiment) |
|-----------------|-----------------------------------|---------------------------------------------------------------|---------------------------------------------------------------------------------|
| 2ML Au on InSb(001) | -36.9 [kJ*mol⁻¹] | Au + 2 InSb → AuIn₂ + 2 Sb ↑ | ΔH = −0.215 eV | 0.5 |
| 2ML Au on InAs(001) | -62.8 [kJ*mol⁻¹] | 3 Au + InAs → InAu₃ + As ↑ | ΔH = −0.007 eV | 3 |
| 2ML Au on InP(001) | -74 [kJ*mol⁻¹] | Au + 2 InP → AuIn₂ + 2 P ↑ | ΔH = 0.172 eV | 0.5 |
| 2ML Au on GaSb(001) | -51.9 [kJ*mol⁻¹] | Au + 2 GaSb → AuGa₂ + 2 Sb ↑ | ΔH = −0.046 eV | 0.5 |
| 2ML Au on GaAs(001) | -94.4 [kJ*mol⁻¹] | 2.5 Au + GaAs → 2.5 Au + Ga + As ↑ | ΔH = 0.701 eV | 2.5(0.4) |
| 2ML Au on GaP(001) | -110.7 [kJ*mol⁻¹] | 5.9 Au + GaP → 5.9 Au + Ga + P ↑ | ΔH = 0.823 eV | 5.9(0.34) |

Table 1: Chemical reactions contributing to the Au nanostructures formation on AIII-BV semiconductor surfaces resulted from 2ML Au deposition at 330°C, as derived from our measurements.

Two regions are visible, one with structures formed of the pure Au phase at the other region (with the
HoF above 80 kJmol⁻¹) where the structures are of AIII-Au alloy. When the system is highly bound
(negative heat of formation), it is difficult to supply for AIII metal (In, Ga) on the surface to form an alloy, so the formed structures phase is made of pure Au.

Conclusions

In conclusion, we have studied the interaction of 2 ML of Au with different AIII-BV (001) semiconductor surfaces at nanoscale. The results showed that all the formed Au-rich nanostructures were crystalline and in epitaxial with AIII-BV substrate. It has been found that the Au diffusion into bulk lattice is very efficient only for the InSb case as it the AIII-BV semiconductor with the lowest binding energy. Furthermore, a difference is observed in the Au interaction with In-rich and Ga-rich semiconductors, as confirmed by machine learning MDS and k-means analysis. The analysis uncovered also that independently of the interaction between Au and AIII-BV semiconductor the main driving force of nanostructures formation is the surface diffusion and nucleation of adatoms produced by the chemical reactions induced by Au atoms on semiconductor surfaces. Our studies also show that the phases formed at nanostructures depend on the AIII-BV semiconductor binding energy (heat of formation). The deeper knowledge of the interaction between Au and AIII-BV semiconductor at atomic level, as presented in our systematic work, will enhance the understanding of the AIII-BV nanowires growth and it will improve the fabrication of new semiconductor electronic devices based of AIII-BV technology.
Methods

Au/AIII-BV sample preparation

N-doped epi-ready indium antimonide – InSb(001), indium arsenide – InAs(001), indium phosphide – InP(001), gallium antimonide – GaSb(001), gallium arsenide – GaAs(001) and gallium phosphide - GaP(001) crystals were mounted on molybdenum plates. Prior to introducing into the UHV Molecular Beam Epitaxy (MBE) system, with a base pressure equal to \(1 \cdot 10^{-10}\) mbar, the samples were rinsed with isopropanol and ethanol and finally dried in a flow of air. The sample temperature is measured by a pyrometer (LumaSense, model IGA 140) with \(\varepsilon=0.55\) for InSb and \(\varepsilon=0.5\) for InAs, InP, GaSb, GaAs and GaP. The substrate surfaces were initially out-gassed for 1h at 150 C. In order to remove oxide layer the samples were exposed of low energy, 700 eV Ar+ ion bombardment at a 60deg incident angle at room temperature (RT). Subsequently substrate surfaces were cleaned at \(T=400\) C (InSb(001)), \(T=427\) C (InAs(001)), \(T=450\) C (InP(001)), \(T=440\) C (GaSb(001)) \(T=500\) C (GaAs(001)), \(T=520\) C (GaP(001)), by using ion beam with the same parameters as parameters to remove oxide layer and then annealing cycles at \(T=450\) C (InSb(001)), \(T=477\) C (InAs(001)), \(T=470\) C (InP(001)), \(T=500\) C (GaSb(001)), \(T=550\) C (GaAs(001)), \(T=570\) C (GaP(001)) were repeated until the c(8x2) InSb(001), (4x2) InAs(001), (4x2) InP(001), (3x1) GaSb(001), c(8x2) GaAs(001), (4x2) GaP(001) reflection high energy diffraction (RHEED) pattern was observed, see supporting information Fig. S3 and Fig. 1a). On such prepared surfaces 2 ML of gold were deposited at exactly the same temperature i.e. 330°C, at a rate of 0.1 ML min\(^{-1}\) as checked by quartz microbalance. After gold deposition samples were cooled down to RT with rate 10 C min\(^{-1}\).
Au/AIII-BV sample characterization and analysis

The samples were transferred at ambient condition to a Dual Beam SEM/FIB FEI Quanta 3D FEG microscope equipped with EDAX EDX/EBSD/WDS microanalysis system for further investigations installed at the Institute of Physics Jagiellonian University Krakow Poland. The size and surface density of developed nanostructures were evaluated from SEM images using free software ImageJ/FIJI[50]. The nanostructure size was calculated as square root of the nanostructure area. The average diffusion radius $r$ i.e. the average distance between nanostructures, was calculated from

$$r = \frac{1}{2} \frac{1}{\sqrt{D}}.$$

The extracted dependencies were presented for AIII-BV semiconductors, which are ordered accordingly to their heat of formation (binding energy) [44], where the most negative value corresponds to the highest bound system. The surface morphologies of the samples were also imaged by the 5500 Agilent Atomic Force Microscope in a tapping mode. Later, the atomically resolved HAADF STEM measurements, where contrast is proportional to atomic number $Z$ and to the sample thickness [51], were performed using a FEI (S)TEM Titan3 G2 60-300 microscope equipped with a monochromator, a probe Cs corrector (DCOR) and the ChemiSTEM technology (X-FEG field-emission electron gun and four windowless detectors Super-X EDX system) [52] operated at 300kV and installed at AGH Krakow Poland. HAADF-STEM images were acquired with a convergence angle of 20 mrad and a probe current of 80 pA. The EDX chemical composition maps were collected using FEI Tecnai Osiris 200kV TEM microscope equipped with ChemiSTEM technology installed at Jagiellonian University Krakow Poland. For the chemical composition determination the Cliff-Lorimier method was used, as implemented in the
manufacturer software ESPRIT from Bruker. For the TEM measurements thin foils (lamellae) were prepared by SEM/FIB dual beam system (FEI Quanta 3D FEG) using a focused ion beam (FIB).

The identification of the formed phases in the examined systems, as verified by calculated phase diagrams by the Materials Project [31-33] and OQMD [53; 54] and also experimental ones [15; 17-19] (see supporting information Fig. S2, Table S2), was based on the analysis of atomically resolved HAADF STEM measurements by examining the interplanar spacing and angles together with the results of the performed EDX experiments and HAADF contrast. The simulations of the identified phases structural models, in the proper zone axis projection, as prepared by a free software VESTA [55], were overlaid on the HAADF experimental data.

The HAADF STEM image quantification was performed for Au/InSb system to distinguish between columns containing Au atoms and pure In-Sb columns (assuming constant sample thickness). The image was segmented into cells containing atomic columns [56; 57]. This has the advantage that all image scattering is associated to some atomic column. Intermixing between the Au and In-Sb phases is studied atomic column-by-column, similar as in [47]. Due to the noise inherent to the experiment, we used Machine Learning algorithms as implemented in Trainable Weka Segmentation [35] to statistically distinguish between these phases, as successively used in HAADF STEM Tomography [58]. Here we used experimental HAADF signal references of pure Au columns (from AuIn$_2$ nanowire) and pure In-Sb column (from bulk). The resulted probability of finding Au is directly proportional to the number of Au atoms in the atomic row (assuming constant sample thickness) and since $\text{Probability}_\text{Au} + \text{Probability}_\text{InSb} = 1$, so the probability of finding Au is directly the Au atoms concentration in the sample (value “1” corresponds to the concentration of 100 atomic %), for details see supporting information (Fig. S1, Table S1).
The determination of the strain fields was performed by Geometric Phase Analysis (GPA) [59] of atomically resolved HAADF STEM images using free software Strain++ [60]. The ellipticity of atomic columns was extracted from atomically resolved HAADF STEM images by free software Atomap [38].

The multivariate statistical analysis of nanostructures parameters by machine learning
Multidimensional Scaling (MDS) [42] and k-means clustering [43] together with Silhouettes scoring [61] for number of clusters estimation was performed using free software Orange [62].

The quantum-chemical calculations of gold build up into InSb lattice were performed by using DFT/GGA with use of the VASP [63-65] code with the following settings: the energy cut-off was set to 400 eV, the sampling of the irreducible Brillouin zone was done according to the Monkhorst-Pack [66] scheme with IBZ sampling in the range of 0.008-0.03 Å⁻¹; the Blöchl’s projector augmented wave (PAW) [67; 68] method for representing valence-core interactions together with PBE [69] functional was employed. The Methfessel-Paxton [70] smearing with σ width of 0.1 eV was used. For solving the Kohn-Sham equations the SCF convergence criterion was an energy change between two successive iterations lower than 10⁻⁵ eV. Geometry optimization parameters were selected in order to get corrections to the forces acting on ions less than 0.001 eV/Å. The cell optimisation was performed via the Birch-Murnaghan equation of state [71]. The model cell was built as the supercell of 1×8×1 (for higher Au concentrations) to 4×8×4 (for lower Au concentrations) primitive InSb unit cells. The thermodynamic functions were taken from the harmonic approximation approach and were verified by the classical Born-Oppenheimer molecular dynamics (MD) based calculations of Gibbs free energy. The MD calculations were performed using Universal Force Field (UFF) with 1 fs time step (sufficient for the systems with heavy atoms and for used temperature), the total time of simulations was equal to 500 ps. The NPT ensemble with Nosé [72] thermostat (T = 330 °C) and Berendsen [73] barostat (p = 0.0 GPa) were used in simulations.
In total we tested ~50 different model configurations of Au incorporation into InSb lattice from which we selected those with the lowest Gibbs free energies.
Author contributions

B.R.J. and A.J. contributed to the characterization of the samples by RHEED/SEM and RHEED/SEM/TEM data analysis and interpretation. A.J. prepared the samples in UHV. A.K., G.C., A.K. and A.C-F. contributed to HAADF STEM measurements. P.I. contributed to the TEM and EDX measurements. B.R.J. contributed to the FIB sample preparation and to the HAADF STEM image quantification by Machine Learning, ellipticity analysis of atomic columns and Machine Learning multivariate statistical analysis of the data. W.P. contributed to the DFT and MD simulation of Au built up into InSb lattice. K.S. contributed to the AFM measurements. B.R.J. prepared the manuscript together with A.J. and F.K. in consultation with all authors. F.K. initiated and organized this project.
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Competing financial interests

The authors declare no competing financial interests.
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Supporting Information

Chemically driven growth of Au rich nanostructures on AIII-BV semiconductor surfaces

B.R. Jany\textsuperscript{a*}, A. Janas\textsuperscript{a}, W. Piskorz\textsuperscript{c}, K. Szajna\textsuperscript{a}, A. Kryshtal\textsuperscript{b}, G. Cempura\textsuperscript{b}, P. Indyka\textsuperscript{c}, A. Kruk\textsuperscript{b}, A. Czyrska-Filemonowicz\textsuperscript{b}, F. Krok\textsuperscript{a}

\textsuperscript{a}Marian Smoluchowski Institute of Physics Jagiellonian University in Krakow, Lojasiewicza 11, 30-348 Krakow, Poland
\textsuperscript{b}International Centre of Electron Microscopy for Materials Science, AGH University of Science and Technology, 30-059 Krakow, Poland
\textsuperscript{c}Faculty of Chemistry, Jagiellonian University, ul. Gronostajowa 2, PL 30-387 Krakow, Poland

\*Corresponding author e-mail: benedykt.jany@uj.edu.pl
Machine Learning HAADF STEM image quantification

The HAADF STEM imaging mode provides structural images where intensities are proportional to both the thickness and mean atomic number $Z[1]$. (Au columns appear brighter than In-Sb columns). By assuming a constant sample thickness, this can be efficiently used to distinguish between columns containing Au atoms and pure In-Sb columns. The image was segmented into cells containing atomic columns$[2; 3]$. This has the advantage that all image scattering is associated to some atomic column. Due to the noise inherent to the experiment, intermixing between the Au and In-Sb phases is studied atomic column-by-column, similar as in$[4]$. Here we used Machine Learning algorithms as implemented in Trainable Weka Segmentation$[5]$ to statistically distinguish between these phases, as successively used in HAADF STEM Tomography$[6]$. For the Trainable Weka Segmentation the following training features were used: mean, median, variance, maximum, minimum. The classes were balanced. The rest settings were set on their default values (classifier: fast random forest of 200 trees with 2 features per tree). The reference areas were used for the Au atomic columns and In-Sb atomic columns, as indicated in Fig. S1a. As a result of image quantification of analysis area (area with Au atom diffusion into the bulk InSb crystal -Fig. S1a) the Au probability map and InSb probability map is computed Fig. S1b-c. Since the probability of finding Au is directly proportional to the number of Au atoms in the atomic row (assuming constant sample thickness) and $\text{Probability}_{\text{Au}} + \text{Probability}_{\text{InSb}} = 1$, so the probability of finding Au is directly the Au atoms concentration in the sample (value “1” corresponds to the concentration of 100 atomic %). The histogram of Au probability (Au atomic concentration) from the area with Au atom diffusion into the bulk InSb crystal is presented in Fig. S1d. Several local maxima are seen Fig. S1d and Table S1. This is compared with EDX measurements of this region as presented in histogram of Au atomic concentration from EDX Fig. 1e and Table S1. The quantitative HAADF STEM shows more local maxima in comparison to the EDX measurements, so in this case in more locally sensitive to the changes of Au atomic concentrations.

| HAADF STEM quantification | EDX measurements |
|---------------------------|------------------|
| Au atomic concentrations  |                  |
| 0.037                     | –                |
| 0.075                     | 0.068            |
| 0.12                      | –                |
| 0.23                      | –                |
| 0.28                      | –                |

Table S1: Au atomic concentration in the area with Au atom diffusion into the bulk InSb crystal as measured by HAADF STEM image quantification and EDX. In this case the quantitative HAADF measurements are more sensitive to local Au concentration then EDX, since more local maxima are visible (value “1” corresponds to the concentration of 100 atomic %).
In Fig. S1f Au probability map (Au atomic concentration) from Area1 is presented, one can see in details that different amount of Au atoms are built up into the In-Sb lattice atomic positions.

Fig. S1: HAADF STEM image quantification of Au/InSb at 330°C. a) atomically resolved HAADF STEM image, Au and InSb reference area marked, b) quantification result, InSb probability map overlaid on HAADF image from analysis area, c) quantification result, Au probability map overlaid on HAADF image from analysis area, d) histogram of Au probability from analysis area. Since the probability of finding Au is directly proportional to the number of Au atoms in the atomic row (assuming constant sample thickness) and Probability_{Au} + Probability_{InSb} = 1, so the probability of finding Au is directly the Au atoms concentration in the sample. e) histogram of Au atomic concentration, as measured by EDX. The obtained Au probability (Au atomic concentration) from HAADF STEM quantification matches well the EDX measurements. The main maxima, corresponding to the main atomic concentrations are marked. It is seen that HAADF STEM is more locally sensitive than EDX since additional small maxima are visible. f) Au probability map (Au atomic concentration) from Area1, one can see in details that different amount of Au atoms are built up into the In-Sb lattice atomic positions. Value “1” corresponds to the concentration of 100 atomic %.
Au-AIII-BV Phase Diagrams

The Au-AIII-BV phase diagrams were calculated from First Principles using the generalized gradient approximation (GGA) approximation to density functional theory (DFT) and the DFT+U extension to it [7; 8] by the Materials Project [9] and also OQMD [10] [11]. In agreement with experimental phase diagrams [12; 13; 14].

Fig. S2: Theoretically calculated Phase Diagrams for Au-AIII-BV systems: a) Au-In-Sb, b) Au-In-As, c) Au-In-P, d) Au-Ga-Sb, e) Au-Ga-As, f) Au-Ga-P, g) Au-In, h) Au-Ga by the Materials Project [9] and also OQMD [10].
| Phase     | Formation Energy [eV] | Phase     | Formation Energy [eV] |
|-----------|-----------------------|-----------|-----------------------|
| AuIn₂     | -0.246                | AuGa₂     | -0.234                |
| Au₃In     | -0.126                | AuGa      | -0.227                |
| Au₇In₃    | -0.141                | Au₂Ga     | -0.151                |
| Au₁₀In₃   | -0.116                | Au₇Ga₂    | -0.102                |
| AuIn      | -0.108                | Au₃Ga     | -0.083                |
| AuIn₃     | 0.016                 | AuGa₃     | -0.023                |

Table S2: Theoretically calculated Phases in the Au-In and Au-Ga system together with their formation energies by the Materials Project[9] and also OQMD[10]. Unstable phases also included. In agreement with experimental phase diagrams[15; 16].
RHEED patterns of the atomically clean and reconstructed AIII-BV surfaces

Fig. S3: RHEED patterns of the atomically clean and reconstructed surfaces of a) (3x1) GaSb(001), b) c(8x2) GaAs(001), c) (4x2) GaP(001), d) (4x2) InAs(001), e) (4x2) InP(001). Main reconstruction spots marked.
Multivariate Statistical Analysis

The obtained from SEM, AFM and TEM measurements data on nanostructures formed in the Au/AlIBV systems are presented in Table S3, as in detailed described in the main article. It is seen that for each AlIBV system a set of seven parameters is used to describe it, forming seven dimensional parameter space. This is later used for multivariate statistical analysis using machine learning Multidimensional Scaling (MDS) and k-means clustering.

| AlIBV system | Average size [nm] | Surface density [1/um²] | Surface diffusion radius [nm] | Average height [nm] | Nanostructure percent under the sample surface [%] | Au concentration in the nanostructure [atomic %] | Number of Au atoms needed to break one AlIBV bound |
|--------------|-------------------|-------------------------|-----------------------------|-------------------|---------------------------------|---------------------------------------------|---------------------------------------------|
| InSb         | 146.3             | 6.1                     | 202.3                       | 8.0               | 35                              | 33.3                                        | 0.5                                         |
| InAs         | 35.9              | 170.5                   | 38.3                        | 7.9               | 0                               | 75.0                                        | 3                                           |
| InP          | 31.4              | 214.4                   | 34.1                        | 11.3              | 6.45                            | 33.3                                        | 0.5                                         |
| GaSb         | 13.1              | 747.4                   | 18.3                        | 0.9               | 69                              | 33.3                                        | 0.5                                         |
| GaAs         | 8.2               | 2003.8                  | 11.2                        | 1.1               | 41.8                            | 100.0                                       | 2.5                                         |
| GaP          | 5.8               | 2088.5                  | 10.9                        | 1.4               | 13.4                            | 100.0                                       | 5.9                                         |

*Table S3: Measured seven parameters of the formed nanostructures in the Au/AlIBV systems.*
Fig. S4: Nanostructures resulted from 2ML Au deposited on InSb(001), GaSb(001), GaAs(001), InP(001) and InAs(001) surfaces at 330°C. Average sizes b), surface densities c) and average diffusion radius d) as a function of the heat of formation of AIII-BV semiconductor. The lines are drawn to guide the eye. Different behavior is observed for the structures grown on In and Ga rich surfaces.
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