

Molecular beam epitaxy and interface reactions of layered GaSe growth on sapphire (0001)

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We have investigated the growth of GaSe, a layered semiconductor, on single crystal $\text{Al}_2\text{O}_3(0001)$ (sapphire), an ionic crystal. We have used reflection high energy electron diffraction, x-ray photoelectron spectroscopy, and transmission electron microscopy and diffraction to study the growth, interface reaction, and resultant film structure. When a clean, heated ($T=620^\circ\text{C}$) sapphire substrate is exposed to Ga and Se from a compound GaSe source (Ga_2Se and Se_2) and a separate uncracked Se source (Se_x , $x\sim 6$), a polycrystalline film is formed with stoichiometry close to that of cubic Ga_2Se_3 . After annealing to 1100°C , the film evaporates, leaving a reacted interface layer containing both Ga and Se. Subsequent deposition on this reacted surface under the same conditions leads to growth of 500–1000 Å grains of layered GaSe, which have their c axis normal to the substrate surface but random orientation parallel to the substrate. A mechanism is proposed that describes the formation of the interface layer and its effect on the subsequent growth of GaSe.

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I. INTRODUCTION

Molecular beam epitaxy (MBE) growth of two dimensional layered materials is often referred to as van der Waals epitaxy (VDWE) because these materials are composed of layers bound together by weak van der Waals forces.¹ GaSe is such a layered material, a semiconductor with a 2.13 eV direct band gap and potential applications in nonlinear optics and photovoltaic. A cubic gallium–selenium compound also exists, Ga_2Se_3 , having a similar band gap (2.6 eV),² but quite different transport and structural properties. A key element of possible future exploitation of these materials is control over which compound forms during heteroepitaxial growth. For growth on covalent semiconductors such as GaAs, both GaSe and Ga_2Se_3 have been reported, depending on the growth conditions.^{3,4} Of particular importance in controlling the structure is the termination and symmetry matching of the substrate. Ga_2Se_3 has not been reported when layered substrates are used. Layered GaSe is formed on cubic GaAs(111) once the interface is passivated by the Se flux through an As–Se exchange reaction, while both GaSe and Ga_2Se_3 may be grown on GaAs(001).³

In this work, we describe the growth of gallium–selenium compound films on sapphire, a transparent, ionic material. We find that deposition of clean $\alpha\text{-Al}_2\text{O}_3(0001)$ at temperatures up to 620°C results in polycrystalline films with a stoichiometry close to that of Ga_2Se_3 . Unlike growth on GaAs, however, remnants of these films remain after annealing to temperatures as high as 1100°C . Another difference from growth on GaAs is that exposure to a pure Se beam does not lead to a strong reaction and/or Se termination of the Al_2O_3 surface. This implies that an interface reaction, possibly based on interdiffusion, occurs between the film and sub-

strate that requires the presence of both Ga and Se. *In situ* reflection high energy electron diffraction (RHEED) and x-ray photoelectron spectroscopy (XPS) studies are used to examine this interface layer, as well as *ex situ* transmission electron microscopy (TEM) analysis. Subsequent deposition on this reacted interface layer leads to the formation of layered GaSe with its c axis parallel to the surface normal. The GaSe films, however, consist of numerous small grains (500–1000 Å) with random rotational orientation parallel to the surface.

II. EXPERIMENTAL PROCEDURE

The sapphire substrates were first cleaned with trichloroethylene, acetone, methanol and rinsed with de-ionized (DI) water; they were then etched in a dilute HF solution, and again rinsed in DI water. The substrates were then blown dry with nitrogen gas, and inserted into the vacuum chamber, where they were thermally cleaned in high vacuum at 1100°C using an electron bombardment heater. All thermal cleaning/annealing cycles were performed in vacuum, and temperature uniformity of the samples appeared to be quite good during heating.

The MBE growth chamber is equipped with GaSe and Se Knudsen cell sources and has a base pressure of 2×10^{-9} Torr. Previous studies have shown that GaSe sublimates as $\text{Ga}_2\text{Se}+1/2\text{Se}_2$ above 500°C ,⁵ while solid Se evaporates as larger molecules, primarily Se_6 .⁶ The molecular beam flux was measured with a crystal thickness monitor, and the GaSe growth rate was maintained at approximately 15 Å/min. The sample temperature was measured using a thermocouple attached to the front side of the sample holder, which was calibrated by comparison to a thermocouple directly attached to a sample surface. The growth temperature was 620°C

unless otherwise noted. The selenium shutter was opened first for 1 min, and then growth was initiated by opening the GaSe shutter for the duration of the deposition (3–5 min). The growth was monitored with a Thermionics/Veetech RHEED system. The diffraction pattern was observed on a standard phosphor screen and recorded with a charge coupled device (CCD) camera for computer enhancement and analysis.

Samples were transferred, in vacuum, between the MBE chamber and an analysis chamber equipped with XPS. XPS spectra using a Mg K_{α} source were obtained before growth, after the initial deposition, after annealing and then after the subsequent deposition. XPS was performed using a Perkin Elmer PHI 560 double pass cylindrical mirror analyzer with the sample normal 45° from the cylindrical mirror analyzer (CMA) axis. Survey spectra are acquired using a pass energy of 100 eV, while detailed scans of the O $1s$, Al $2p$, Ga $3d$, and Se $3d$ regions are acquired using a pass energy of 25 eV. The binding energy scale was calibrated by assigning a value of 531.6 eV to the O $1s$ core level peak associated with the substrate.⁷ Spectra were fitted to Gaussian-broadened Lorentzians and a linear background using a least-squares minimization routine. For the Ga (Se) $3d$ spectra, spin-orbit pairs with splittings of 0.56 eV (0.86 eV) and ratios of 0.667 were used. The fits were made with a constant Lorentzian full width at half maximum (FWHM) of 0.56 eV for Ga $3d$ and 0.36 eV for Se $3d$.⁸

The substrates were prepared from optically polished sapphire wafers cut to about $9 \times 9 \text{ mm}^2$. The experimental procedure was as follows: Al_2O_3 substrates were thermally cleaned at 1100°C and then analyzed with XPS (I). Approximately 30 \AA of Ga_xSe_y was then deposited on the samples, which were then characterized with XPS (II). Samples were then thermally cleaned with the electron beam heater at a series of increasing temperatures from 950 to 1100°C . After each anneal the samples were cooled and transferred in vacuum into the XPS chamber for chemical analysis. After the final anneal (1100°C) and chemical analysis (III), the samples were transferred back into the growth chamber for further deposition experiments. The subsequent deposition was carried out with the same conditions as the initial deposition. The growth was again monitored *in situ* with RHEED and XPS (IV), after which *ex situ* TEM/transmission electron diffraction (TED) analysis was performed.

III. RESULTS

Structural and chemical properties of the samples were studied using RHEED and XPS. Figure 1 shows XPS survey spectra of a sample at various stages of processing. As were defined above, the Roman numerals I, II, III, and IV represent samples analyzed after: the initial thermal cleaning, initial deposition, thermal annealing at 1100°C , and subsequent deposition, respectively. Spectra III clearly shows the presence of Ga and Se even after thermal annealing up to 1100°C . Substrate peaks (O $1s$, Al $2s$, and Al $2p$) can also

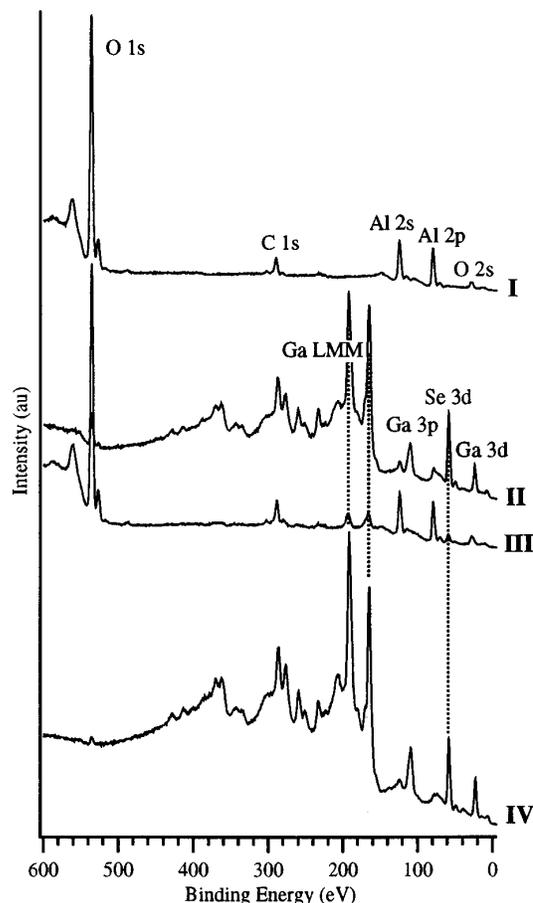


FIG. 1. XPS survey spectra taken after various processing steps. (I) is the initial, thermally cleaned sapphire substrate, (II) is after the initial GaSe deposition, (III) is taken after the sample was thermally annealed to 1100°C , and (IV) is taken after the subsequent GaSe deposition. Notice the presence of Ga and Se peaks even after the 1100°C annealing in (III).

be seen in spectra II and IV. Based on the attenuation of these peaks, the film thicknesses are estimated to be about 30 and 50 \AA , respectively.

High resolution XPS spectra of the Ga $3d$ and Se $3d$ core levels are shown in Fig. 2. The experimental data points are shown as filled circles, and the sum of the individual peak fits is shown as a solid line through the data points. Spectra III of Fig. 2 clearly show that there are still traces of Ga and Se present after the 1100°C anneal; the additional peak at 23.2 eV is the O $2s$ core level emission from the substrate. The line shape is fitted quite well with a symmetric Voigt profile, and not the asymmetric Doniach–Sunjic line shape.⁹ This is an indication that the gallium present is chemically bonded at the interface, and not present as unreacted islands of metallic gallium on the surface. The Ga peak associated with the initial deposition is 0.4 eV higher in binding energy than for the subsequent film. The Se $3d$ core level experienced very little energy shift as a result of the processing; all of the Se $3d$ core level peaks were fit to a binding energy of 54.6 eV , within an error of 0.1 eV . The difference in binding

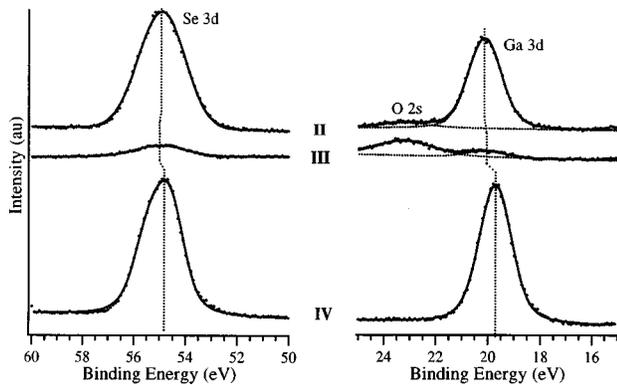


FIG. 2. High resolution XPS spectrum of Ga and Se 3d core level emission taken after various processing steps. (II) is after the initial GaSe deposition, (III) is taken after the sample was thermally annealed to 1100 °C, and (IV) is taken after the subsequent GaSe deposition.

energy between the Ga and Se peaks in the two is indicative of a different chemical compound and/or local structure for the two cases. The splitting for bulk GaSe is 34.8 eV, consistent with the subsequent deposition, while that for bulk Ga₂Se₃ is 34.7 eV.⁷

Although there are no clear chemically shifted components in the overlayers, information can be obtained from a measurement of the peak width. Gaussian broadening is a result of photoemission from atoms in different structural and chemical environments, thus the peak width is an indication of the crystalline uniformity of the film. The Ga 3d peak associated with the initial deposition has a FWHM of 1.41 eV, while the subsequent deposition has a width of 1.36 eV. By comparison, the peak width of the Ga 3d core level for a single crystal sample of GaSe was measured at 1.23 eV. The FWHM of the Se 3d core level of the initially deposited film is 1.71 eV, while the width for the subsequent deposition is 1.32 eV. The Se 3d core level width of the single crystal is 1.12 eV. This is an indication that the subsequent film is substantially more homogeneous than the initial deposition, but is still less ordered than a single crystal.

The stoichiometry of the films may be estimated from the relative intensities of the various photoemission peaks, referred to the value for a single crystal GaSe sample. The stoichiometry of the deposited films was found to be Se rich in all cases. The initial film had a Se to Ga ratio of 1.65 ± 0.09, which is close to the stoichiometry of Ga₂Se₃; the subsequent deposition had a Se:Ga ratio of 1.07 ± 0.04, consistent with GaSe. The extra ~10% Se in both cases may be due to a Se-rich interface region. Annealing the initial films to form the reacted interface layer increases the Se:Ga ratio from 1.65 to 2.90 for the film annealed to 1100 °C, although the latter number has large error due to the low emission intensities.

The substrate also undergoes a significant change during the initial deposition and anneal. Assuming an initial stoichiometric O:Al ratio of 1.5, the initial deposition decreases that by about half to 0.7. This could arise from Al segregation into the overlayer and/or Se replacement of oxygen in the substrate. After annealing to remove the film, the O:Al

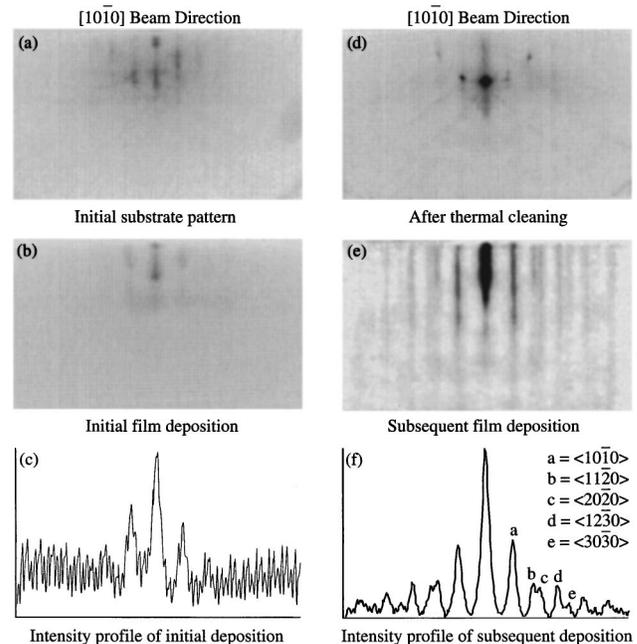


FIG. 3. Experimental RHEED patterns of (a) the initial substrate, (b) the initial film, (d) the annealed film, and (e) the subsequently deposited film. Intensity profiles of the initial and subsequently deposited films are given in (c) and (f), respectively. Notice the superposition of diffraction from multiple domains in (f), labels (a)–(e) denote the origin of the individual diffraction streaks.

ratio returns to a nearly stoichiometric 1.43. After the subsequent deposition the O:Al ratio is gain reduced, although overlap between the Ga and Se plasmon lines and the substrate Al emission makes quantification difficult.

The structure of the films was monitored *in situ* with RHEED after each processing step. Sapphire(0001) and GaSe(0001) are hexagonal surfaces with a lattice mismatch of about 21%. Figure 3 shows RHEED diffraction patterns for the beam directed along the substrate $[1\bar{1}\bar{2}0]$. Frames (a), (b), and (c) summarize the initial deposition: (a) is the pattern for the thermally cleaned substrate; (b) is the pattern after 3 min (approximately 30 Å) of deposition; while (c) is a plot of the diffraction intensity summed along the vertical direction. Similarly, frame (d), (e), and (f) summarize the subsequent deposition. The subsequent deposition clearly has better crystallinity than the initial deposition, as can be seen by the increased sharpness and intensity of the diffraction pattern. Analysis of the streak spacing of the subsequent film gives a lattice constant of 3.73 ± 0.03 Å which is consistent with stoichiometric GaSe (3.76 Å). Measurements on our system for a GaSe single crystal gave 3.75 ± 0.02 Å. Although the initial film is difficult to analyze, a lattice constant of 3.96 ± 0.13 Å is obtained, which is closer to the expected atom spacing for the (111) surface of Ga₂Se₃ (3.83 Å) than to that of GaSe.

The multiple streaks demonstrate the presence of multiple orientations, as noted in Fig. 3(f). The diffraction patterns in Figs. 3(b) and 3(e) do not change when the sample is rotated about the surface normal. The absolute intensity changes slightly, but the structure does not. The diffraction pattern is

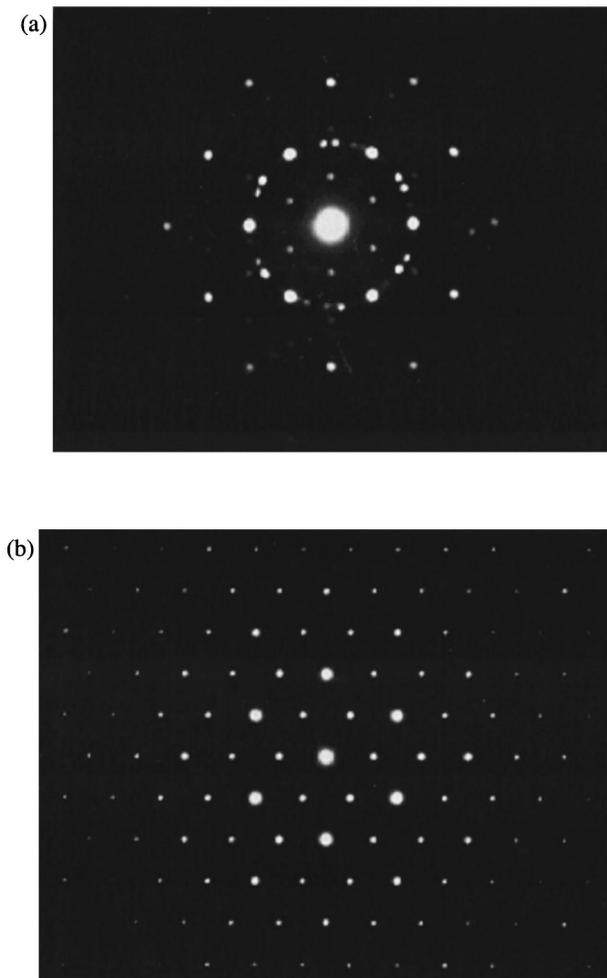


FIG. 4. TEM micro diffraction pattern from (a) the subsequently deposited film, and (b) from a single crystal GaSe standard. Four distinct patterns of the (0001) zone axis of GaSe can be seen with random rotations about the surface normal.

a superposition of diffraction from the various grains in the 1 mm \times 5 mm area of the electron beam on the surface. The absence of variation in the pattern with rotation suggests the following: first, the grain size is small compared to the size of the electron beam; second, the grains have no preferred rotational alignment with respect to the surface normal.

Transmission electron microscopy and diffraction was used to determine the grain size and confirm RHEED findings. TEM sample were prepared by ion beam milling from the backside of the substrate. Figure 4(a) is a micro diffraction pattern of the subsequently deposited film; this pattern was obtained from a portion of the sample where the substrate was milled completely away. The spot size for the micro diffraction is about 1000 Å, and clearly shows four identical patterns with random rotations about the (0001) zone axis. Figure 4(b) is a diffraction pattern taken from a single crystal GaSe sample for comparison. The pattern is in agreement with the theoretically calculated diffraction pattern for either beta or epsilon GaSe along the (0001) zone axis—the exact polytype could not be distinguished with this analysis. The lattice parameter deduced from Fig. 4(a) is a_0

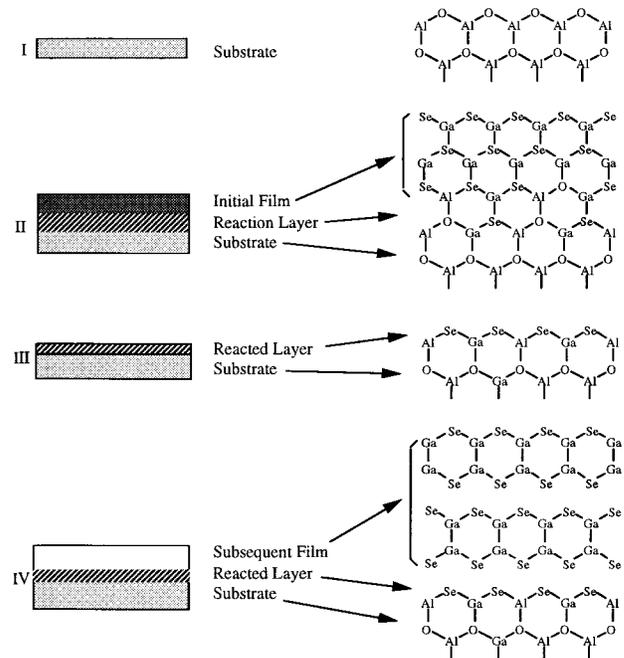


FIG. 5. Schematic representation of the interface reaction which takes place at the growth interface. A schematic of the interface is given after each major processing step: the initial substrate surface (I), the initial film interface (II), the surface after the initial film has been thermally annealed (III), and the interface after the subsequent growth.

$=3.80 \pm 0.03$ Å. Given the number of distinct patterns observable and the size of the electron beam, the grain size is estimated to be on the order of 500–1000 Å.

These observations have been made on (1120) sapphire substrates as well, but the best quality films have been obtained with sapphire(0001) substrates.

IV. DISCUSSION

The structure and composition of a Ga_xSe_y film grown on sapphire(0001) is strongly dependent on the initial condition the Al_2O_3 surface. Exposing a clean surface to a Se and Ga flux results in polycrystalline films with a stoichiometry and lattice parameter close to that of Ga_2Se_3 than GaSe. Ga_2Se_3 has a cubic zinc-blende structure with a lattice parameter of 5.418 Å.¹⁰ The (111) surface of Ga_2Se_3 has hexagonal order and a reciprocal lattice spacing which is only 2.2% smaller than the c plane of GaSe; this make it difficult to distinguish between the two materials with RHEED observations alone. It is also possible that the film has a similar structure to that of the corundum substrate, although that structure is not known to exist for a Ga–Se compound. The weak RHEED patterns and broad XPS peaks imply a nonuniform film with a variety of local environments for both the Se and Ga atoms.

The persistence of Ga and Se even after annealing the sample to 1100 °C, is an indication that there is a strong interface reaction in which Ga and Se are involved in covalently bonding in the interface layer. Figure 5 is a schematic representation of the interface layer which is formed between the film and substrate. It is not known whether this

layer forms during growth or in the subsequent anneal, since the shift in XPS binding energies is too small to measure an interface component from a thick film. Since growth on this surface is different after the anneal, however, the structure must undergo some sort of change at the elevated temperatures.

The variation in both O:Al and Ga:Se ratios with processing imply a significant exchange reaction at the interface. The reduced O:Al ratio after deposition implies outdiffusion of Al into the overlayer as well as a Se–O exchange in the substrate. The excess Se in the films beyond the stoichiometric Ga₂Se₃ could be due either to an absence of Ga as it is replaced by Al or a deeper burial of Ga in the substrate than Se. Ga and Al ions have very similar chemical and physical properties, and as a result they are very soluble in most compounds containing the other species. The net result is that the measured Ga:Se ratio of the film is selenium rich and the substrate is oxygen deficient near the interface. As the samples are annealed to higher and higher temperatures, the Se to Ga ratio increases, and the O to Al ratio increases towards the stoichiometric value.

No significant shifts of the XPS core level energies were found for the interface reacted layer. Since the electronegativity of Al is only slightly higher than Ga, there may not be significant shift in the SE binding energy due to the Se–Al bond formation at the interface. However, there is a significant difference in the electronegativities between O and Se (25%); Ga and Al core levels should be effected by this difference, particularly in the interface region, but little was observed. This may be due to the level of attenuation of the interface peaks, or to differing levels of ionic bonding character.

Although the interface layer contains about three times as much Se as Ga, Ga plays an important role in the interface reaction. Deposition of pure selenium on the sapphire substrate does not lead to a stable Se surface layer. An amorphous film of Se was deposited on the surface at room temperature, but desorbed after a week in ultrahigh vacuum (UHV) conditions. Selenium deposition was attempted at higher temperatures as well, up to 650 °C, but no selenium adsorbed at these elevated temperatures. It is only when gallium is present that we have observed selenium to react with the sapphire surface. This behavior has also been observed with SnSe₂ on sapphire in another unpublished work.¹¹

RHEED data show that the subsequent deposition of GaSe has significantly better crystal quality. We believe that this is a result of the reaction and restructuring of the substrate surface, possibly making the surface less polar. Previous studies have shown that single domain growth of GaSe on GaAs could be obtained only after terminating surface dangling bonds.³ However, with the same number of valence electrons in O and Se or in Ga and Al, simple substitution will not lead to automatic passivation in this case. The GaSe structure consists of two dimensional layers with two sheets of Ga sandwiched in-between two sheets of Se. The Se outer sheets interact with neighboring sheets via van der Waals forces. The ideal substrate for GaSe is then one with no

dangling bonds or strong ionic interactions. The reduced ionicity of Se relative to O may lead to a less reactive surface that is more suitable for van der Waals interactions. The polar surface of Al₂O₃ appears to promote the growth of Ga₂Se₃.

The photoemission and TEM/TED results are consistent with the RHEED results for the subsequent film. In XPS, the separation between the Ga and Se 3*d* peaks is the same as that for single crystal GaSe, while the peaks are slightly broader. The slight variations in energy may result from regions near grain boundaries. The stoichiometry is slightly Se rich, which may be reflective of the Se-rich interface region, or it could also be due to excess Se at grain boundaries. As stated earlier, the TED results indicate randomly oriented grains of size 500–1000 Å.

The XPS results for the initial deposition show a different separation (about 0.4 eV smaller) between the Ga 3*d* and Se 3*d* peaks than for the subsequent deposition. Although there is no report of the separation for Ga₂Se₃ in the literature, the reduction is consistent with what would be expected from the change in charge distribution between the two crystal structures.

V. SUMMARY

GaSe thin films have been grown on sapphire (0001) substrates overcoming a lattice mismatch of 21%. Surface reconstruction has been accomplished by first depositing an initial film of Ga_xSe_y, and then annealing the film at high temperature. The annealing step removes most of the initial film and activates a surface exchange reaction in which oxygen and aluminum intermix with selenium and gallium at the interface. Crystalline growth of GaSe is then possible on this reacted surface. Stoichiometric GaSe films grow with the *c* axis parallel to the surface normal; grain sizes are on the order of 500–1000 Å, and have random rotations about the surface normal.

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