Structure of epitaxial Gd\textsubscript{2}O\textsubscript{3} films grown on GaAs(100)

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(Received 6 April 1999)

Single-crystal Gd\textsubscript{2}O\textsubscript{3} films were grown epitaxially on GaAs(100) substrate. From the single-crystal momentum space analysis on four different samples, 185, 45, 25, and 18 Å thick, a Mn\textsubscript{2}O\textsubscript{3} isomorphous cubic structure is identified. The Gd\textsubscript{2}O\textsubscript{3} film aligns its twofold (110) axis with the fourfold (100) surface normal of the substrate, while aligning its [001] and [T10] axes with the [011] and [011] axes of GaAs within the plane, respectively. The absence of the other possible twofold growth orientation can be explained by the bonding configuration at the interface. The 18- and 25-Å-thick samples show an elastically strained component in the film, while thicker samples appear fully relaxed, probably through misfit dislocation formation. [S0163-1829(99)08439-8]

I. INTRODUCTION

Reliable passivation layers on semiconductors are becoming increasingly more critical as the device sizes continuously decrease. In the case of silicon passivation, amorphous oxide layers have performed well in submicron devices. Smaller devices (on the order of 0.1 μm or less) require thinner oxide layer thickness, which is now approaching a dimension of several atomic layers. Limitations on the conventional oxide have prompted an intensive search for better gate dielectrics to be used in such a regime. Among them, a defect-free and thermodynamically stable single-crystal oxide film layer may best fulfill the requirements for such small transistors. For GaAs, a successful surface passivation remained as an unsolved key issue in compound semiconductor technology for the past three decades, until our discovery of an amorphous oxide mixture of Ga\textsubscript{2}O\textsubscript{3}(Gd\textsubscript{2}O\textsubscript{3}).\textsuperscript{1} Recently, we have discovered\textsuperscript{2,3} an epitaxial single-crystal Gd\textsubscript{2}O\textsubscript{3} film as another excellent candidate for the GaAs(100) surface passivation.\textsuperscript{4} In this paper, we focus on the structural studies of Gd\textsubscript{2}O\textsubscript{3} films using single-crystal x-ray diffraction.

II. EXPERIMENT

A triple-axes, four-circle goniometer and a 12-kW rotating anode x-ray source are used in our study of the reciprocal space. A pair of flat graphite crystals are used to monochromatize and analyze the Cu K\alpha x-ray beam, with a resolution of 0.01 Å\textsuperscript{−1} along the longitudinal and 0.005 Å\textsuperscript{−1} along the transverse directions, respectively. The low resolution is chosen intentionally in order to increase the sensitivity to very thin films and make the search in reciprocal space less tedious. The distinct advantages of the triple-axes geometry are the significantly improved separation of θ and 2θ components and the resulting simplification of the data analysis. In a more widely utilized double-crystal geometry, θ resolution is typically about a degree wide, which can cause significant misinterpretations when the films exhibit simultaneously true mosaic features like dislocation caused broadening, layer tilts, and a distribution of layer spacings.

Measurements reported here were carried out in ambient air, where there was no measurable film degradation, in agreement with earlier studies.\textsuperscript{3}

III. RESULTS

In the single-crystal geometry scans were first carried out along the surface normal direction. Here, a broad peak near 2θ=47.5° was identified in 185-, 45-, 25-, and 18-Å-thick Gd\textsubscript{2}O\textsubscript{3} films, as shown in Fig. 1. The intensity of this diffraction peak increased while the peak widths decreased with the film thickness, suggesting that it was originating from the epitaxial film. In addition, the peak position shifted towards larger diffraction angles for thicker films, typical to a strain relaxation in the film. All these features were typical characteristics of a strained layer epitaxial film growth. The peak widths in these 2θ-θ scans are a direct measure of the inverse correlation lengths perpendicular to the surface. In a defect-free unstrained epitaxial film, this correlation length corresponds to the film thickness, and the peaks broadened only by the finite-size effect. In a strained and/or defective film, however, a distribution of layer spacings may introduce an additional peak broadening. A separation of the strain-caused broadening and the finite-size caused broadening is often very difficult, especially for thin films with low count rates and only few accessible Bragg peaks. A careful analysis of the intensity distribution around a few diffraction peaks in reciprocal space, however, is often sufficient to extract substantial structural information.

The layer spacing, as determined from the position of the peak near 2θ=47.5, decreases from 2.015 to 1.914 Å, with increasing film thickness. This change in layer spacing indicates a 5.5% strain relaxation in the film, as shown in Fig. 2(a). Here the strain assumes a zero value at the bulk layer spacing of 1.911 Å or (440) of α-Gd\textsubscript{2}O\textsubscript{3}, as we will explain later. The widths of the peaks in Fig. 1 are plotted in Fig. 2(b). The 18-Å film exhibits a defect-free region of about 9 Å. The 25-Å film gives a 26-Å correlation length, meaning an essentially defect-free film, while 45- and 185-Å films exhibit 34- and 122-Å correlation lengths, respectively.
The θ-rocking or mosaic scans of these peaks at their maximum 2θ positions reveal important information about the nature of defects in the film. A film with defect-free atomic layers, perfectly aligned with the substrate layers yields a sharp peak width identical to that of the substrate peaks, limited by the instrument resolution. The presence of defects, like misfit dislocations, introduces a pronounced mosaic broadening. Figure 3 shows the mosaic scans of these four different films. The 18-Å film shows a single sharp peak with a width of full width at half maximum (FWHM) 50.39°, which is slightly above the instrumental resolution of 0.25°, while the 25-Å film displays a sharp peak (FWHM 50.36°) superimposed on a broader peak. For thicker films ~45- and 185-Å films!, the sharp component disappears, but the broad component persists. The broad component has a width of 3.8° when it first appears in the 25-Å film, but gets narrower with increasing thickness; 3.25° and 1.82° for 45- and 185-Å films, respectively. This we interpret as a fully strained epitaxial growth for the film with a thickness not exceeding 18–25 Å. The broad peak is associated with misfit dislocations, and its width results from the strain fields that exist around individual dislocations. This strain field decays rapidly with distance. It is therefore natural to expect that the thinner films will be most affected since all atoms would experience this strain field in some form. As thickness increases, misfit dislocations and their strain fields would be buried deep at the interface, and the peak widths would gradually decrease, in agreement with our observations.

The level of strain buildup or elastic distortion in the film is directly proportional to the bulk lattice constant difference of the film and the substrate. Thin films can accommodate large elastic strains, but as the thickness increases it becomes energetically more favorable to create misfit dislocations, or discommensurations at the interface that relax the elastic distortion of the film at a critical thickness. As an example, for the In_xGa_{1-x}As/GaAs (~100) system the critical thickness varies from 10 to 1000 Å for a strain of 0.07–0.003. These empirical values are in good agreement with the theory. The measured strain in our 18-Å film is about 0.06, from direct comparison of the peak positions of the 18- and 185-Å films shown in Fig. 1. Here, we assume that the 185-Å film is fully relaxed and assumes the bulk structure of a cubic phase as we will identify next. Interestingly, our assigned critical thickness value in the range 18–25 Å qualitatively agrees with the one found for the In_xGa_{1-x}As/GaAs(100) system.

In order to associate the film diffraction peak in Fig. 1 with a particular structure, we examined all known Gd_2O_3 structures that are monoclinic, hexagonal, and cubic structures. For the peak position, we found a good agreement with the ~440! peak of the a-Gd_2O_3 cubic structure. The measured lattice constant of 10.83 Å agreed well with the bulk form of this cubic phase which has a 10.813-Å lattice constant, belongs to the space group Ia3, and is an isomorph of the Mn_2O_3 structure. This assignment fixed the 110 direction of the film parallel to the surface normal, or [001] direction of the GaAs substrate. In order to find the relative inplane orientation, we searched for 222 strong reflections of the film on a cone centered around the [110] Gd_2O_3 axis or [001] GaAs axis, i.e., 360° φ scan with a 35.26° χ tilt (the angle between film [111] and [110]). As expected, this scan revealed two 222 peaks at 0° and 180° φ.
angle at the right lattice spacing. This established an in-plane epitaxial relationship as $[001]_{\text{Gd}_2\text{O}_3} / [011]_{\text{GaAs}}$ and $[\overline{1}10]_{\text{Gd}_2\text{O}_3} / [01\overline{1}]_{\text{GaAs}}$. Figure 4 shows this cone scan. With the twofold $[110]$ film axis aligned along the substrate four-fold axis, epitaxial films were expected to satisfy epitaxial conditions in two degenerate orientations. Interestingly, the Gd$_2$O$_3$ films, however, were only growing in one of the two possible orientations with no trace of the other orientation.

We have also carried out scans along all the major zone axes, and searched for peaks that belonged to a second phase. These included specific lattice spacing searches that belonged to the monoclinic and the hexagonal phases. We could not find any evidence for any phase formation other than the cubic phase, in agreement with our in situ reflection high-energy electron diffraction observations.\textsuperscript{2,3} We next searched for other peaks that belong to the cubic $\alpha$ phase. All the peaks measured were at their predicted positions. Figure 5 shows some of these major diffraction peaks in reciprocal space where $H$, $K$, and $L$ refer to the Gd$_2$O$_3$ indices. The measured peak intensities of these peaks are tabulated in Table I, and are compared to values taken from the powder diffraction files. Remarkably, the measured intensity values agreed well with the ones listed for the cubic phase. Observed small deviations in some of the intensities remain within our measurement statistics and analysis errors, considering that no geometrical corrections were made to our data due to the sample geometry. This approximation only

![FIG. 3. Mosaic or $\theta$ scans for the four different thicknesses Gd$_2$O$_3$ film samples find two distinct peak shapes coexisting near 25 Å thickness, a clear indication of strain relaxation through misfit dislocations.](image)

![FIG. 4. The 360° $\phi$ scan of the 185 Å finds only one pair of $\{222\}$ peaks for the Gd$_2$O$_3$ film indicating a single-crystal growth.](image)

![FIG. 5. The measured diffraction peaks of the $\alpha$-Gd$_2$O$_3$ phase. $H$, $K$, $L$ refers to the reciprocal lattice of this phase.](image)

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remains valid within a range of diffraction angles where the sampling volume does not vary significantly.

IV. DISCUSSION

The cubic $\alpha$ phase of Gd$_2$O$_3$ has a large unit cell $a = 10.79\,\text{Å}$ compared to that of the GaAs $a = 5.653\,\text{Å}$. As shown in Fig. 6, the lattice matching conditions of the epitaxial growth are satisfied over unusually long lengths at the interface. In one direction $[011]$ of GaAs, it takes about $32.58\,\text{Å}$ (with a $1.9\%$ lattice mismatch), and in another, $[0\overline{1}1]$ GaAs direction, it takes about $15.35\,\text{Å}$ (with a $3.9\%$ lattice mismatch) to match the unit cells. The observed $5.5\%$ strain buildup in thin films, measured from the film layer spacing (Fig. 2), is unusually large, and cannot be explained by the observed in-plane lattice mismatch values alone. This is a clue that something unusual is taking place at the interface, which is causing this additional distortion in the size and shape of the equilibrium unit cell. This can be caused by a grossly distorted covalent bonding of atoms at the interface.

It is unlikely that interatomic forces acting over $32.58$- and $15.35\,\text{Å}$ distances can be responsible for this supercell epitaxy. This is especially true during the initial stages of the growth, when there are too few Gd and O atoms on the surface even to complete a single unit cell. Since the epitaxial growth starts with nucleation at many different sites across the substrate surface, the overall film growth will not be coherent but will compose of single-crystalline regions that have a shifted phase relationship with respect to each other, forming so-called antiphase boundaries in between. As the unit-cell matching length increases, the number of possible nucleation sites or density of antiphase boundaries is expected to increase in proportion. In addition to this large
degree of degeneracy for possible nucleation sites, in the Gd₂O₃/GaAs(100) case there is a rotational degeneracy: the (110) twofold planes of the film, in principal can satisfy the same epitaxial relations in two different orientations on the fourfold symmetric (100) planes of the substrate. Remarkably, the system chooses only one orientation, and grows with a high structural perfection.

In the case of molecular beam epitaxy growth of II-VI compounds on GaAs, the interface chemistry can be successfully studied by the consideration of valence electrons of the surface compounds. Typically, the excess of valence electrons can lead to a distortion of the tetrahedral configuration of the bonding at the interface, and can change the number of bonds from four to three or two. In the tetrahedral bond configuration, GaAs has four valence electrons per atom. In the Ga₂O₃ sesquioxide, the Ga atom contributes three valence electrons and the O atom contributes six electrons to a Ga-O bond. This results in an extra electron, which makes the tetrahedral configuration in Ga₂O₃ unstable. A tetrahedral Ga-O bond. This results in an extra electron, which makes the Ga₂O₃ sesquioxide, the Ga atom contributes three valence electrons and the O atom contributes six electrons to a Ga-O bond. This results in an extra electron, which makes the Ga₂O₃ sesquioxide, the Ga atom contributes three valence electrons and the O atom contributes six electrons to a Ga-O bond. This results in an extra electron, which makes GaAs a semiconductor.

Once the positions of the As atoms at the interface are assigned to that of the O atoms, the puzzle of single-crystal growth is essentially solved. This will fix the positions of the oxygen atoms in the Ga₂O₃ lattice growing on this template. The (110) plane of the bulk phase of the α-Gd₂O₃ has a similar configuration for the oxygen atoms. So far, we have explained the interface structure and the epitaxial growth but have not explained why the system chooses only one orientation out of two possible ones for the epitaxial growth. For this, we have to look at the second layer of atoms and beyond. Here, Gd atoms form the same rows as the O atoms, but now there are one quarter less Gd atoms compared to the O atoms. As a result, oxygen atoms are rearranged along the rows to accommodate these missing Gd atoms. This significantly distorts the bonds and displace the O atoms from their tetrahedral sites toward their equilibrium positions in the bulk Ga₂O₃ structure. Since every O atom is bonded to two Ga atoms at the interface, its displacement would involve bond stretching and bond bending. The two degenerate growth orientations, therefore, distinguish themselves as being either predominantly bond bending or bond stretching. Since displacement of oxygen atoms along the rows shown would involve primarily bond bending, this should be energetically favored over the alternative degenerate orientation that primarily favors stretched Ga-O bonds, as shown in Fig. 6.

The Gd₂O₃ epitaxial films on GaAs(100) are also interesting for studying the dislocation formation. These films experience very different forces along the two in-plane directions. Along the [011] GaAs direction it is under a large tensile strain (~3.9%), while in the orthogonal direction it experiences a compressive strain (1.9%). If strain relaxation takes place through the creation of misfit dislocations, these dislocations are expected to be uniaxial. In a likely scenario, uniaxial dislocations may form separately in both the substrate and the films but substrate ones would be orthogonal to film dislocations. These important and interesting issues may find answers through further studies of this system by high-resolution electron and high-resolution x-ray diffraction experiments.

ACKNOWLEDGMENTS

We thank D. Murphy, R. Tung and R. M. Fleming for valuable discussions.