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Crystallographic Relationships Between GaAs, As and Ga₂O₃
at the GaAs-Thermal Oxide Interface

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ABSTRACT

The morphology and distribution of phases resulting from the thermal oxidation of GaAs at 500°C has been investigated by application of high-resolution transmission electron microscopy to cross-sectioned specimens. The oxide layer grown at 500°C was found to consist of epitaxial γ -Ga₂O₃ with hexagonal As precipitates at the interface with GaAs. The evolution of the oxide/GaAs interface morphology is discussed in light of these results.

INTRODUCTION

The thermal oxidation of GaAs became a subject of great interest in the 1970's when the feasibility of producing metal-insulator-GaAs devices was being explored. The microstructure and chemical composition of thermal oxides have been exhaustively investigated by x-ray diffraction, Auger depth profiling, x-ray photoelectron spectroscopy, conventional transmission electron microscopy and several other techniques. The findings of these studies are reviewed in articles by Schwartz [1], Thurmond et al [2] and Wilmsen [3].

Since the bulk of this work was reported, many advances in materials characterization techniques have been made. In particular, the spatial resolution of transmission electron microscopes has improved to the atomic level [4] and methods for the preparation of cross-sectional specimens have been developed [5,6]. In this letter, the results of a high-resolution transmission electron microscopy study of the thermal oxide on GaAs are reported. Emphasis is placed on microscopic phase identification and the determination of orientation relationships, topics which are not easily addressed with any other technique.

EXPERIMENTAL

Gallium arsenide (100) wafers (Si-doped to $3.6 \times 10^{18} \text{ cm}^{-3}$) were chem-mechanically polished with sodium hypochlorite. After high energy proton implantation (300 kV, 10^{16} cm^{-2}) the wafers were annealed at temperatures between 300 and 600°C in flowing argon (with residual O_2 and water vapor). The wafer annealed at 500°C for 15 minutes was chosen for detailed study. As oxidations in various atmospheres such as dry O_2 , wet O_2 and air have been shown to yield similar results [3], it is expected that the morphology and crystallographic features of the oxide chosen for this study will be representative of other thermal oxides grown at the same temperature. It is clear, however, that the results reported here may differ quantitatively from the results (e.g. oxide thickness and quantity of phases) obtained from thermal oxides grown under different conditions.

Cross-sectional specimens were prepared by forming a sandwich with epoxy, followed by mechanical polishing and then argon ion milling in a specimen stage cooled by liquid nitrogen. High resolution images were recorded in $\langle 110 \rangle$ GaAs zone-axis orientation with a JEOL JEM 200CX operated at 200 keV (interpretable point-to-point resolution ~ 0.23 nm).

RESULTS AND DISCUSSION

1. The γ -Ga₂O₃/GaAs orientation relationship

Figure 1(a) is an image of the GaAs surface region after oxidation. The indexed diffraction pattern from the same region is shown in Fig. 1(b). The 044 and 004-type reflections from cubic γ -Ga₂O₃ are clearly visible and indicate a strongly preferred orientation relationship with the GaAs substrate. The high magnification image of Fig. 1(c) confirms this result. The $\{111\}$ lattice planes of γ -Ga₂O₃ ($a_0 = 0.822$ nm [7], a_0 (measured) = 0.824 ± 0.008 nm) are resolved and the corresponding diffraction spots are faintly visible in Fig. 1(b). These results show that the γ -Ga₂O₃ phase is epitaxial with the simple orientation relationship

$$\begin{aligned} \{111\}_{\gamma\text{-Ga}_2\text{O}_3} &|| \{111\}_{\text{GaAs}} \\ \langle 1\bar{1}0 \rangle_{\gamma\text{-Ga}_2\text{O}_3} &|| \langle 1\bar{1}0 \rangle_{\text{GaAs}} \end{aligned}$$

Deviations from this orientation relationship by up to 5° were detected by lattice imaging in some regions of the oxide film.

It is interesting to note that if the lattice correspondence of two (hkl) planes of γ -Ga₂O₃ with three (hkl) planes of GaAs is

considered, the lattice mismatch is only 3%. This high degree of lattice correspondence is the probable cause for the formation of the β phase in place of the bulk equilibrium γ phase (monoclinic) of Ga_2O_3 . X-ray diffraction [8-10] and electron diffraction [8,11,12] studies reported in the literature claim that Ga_2O_3 is present as only the β phase. It is plausible, however, that a thicker oxide might contain only a thin interfacial layer of the γ phase with the remainder in the β form. In this case the volume fraction of the γ phase might fall below the detection limit of x-ray techniques. In any case, the conditions for formation of the γ phase remain to be determined.

2. The hexagonal arsenic/GaAs orientation relationship

Two distinct oxide/GaAs interface morphologies were observed. In some areas, oxidation-enhanced decomposition of the GaAs resulted in the formation of voids at the interface (see Fig. 1(a)). No trace of crystalline As or As_2O_3 was detected in the immediate vicinity of these voids. However, in the regions between voids the oxide/GaAs interface was found to contain a high density ($2-5 \times 10^{11} \text{ cm}^{-2}$) of small (5-10 nm in diameter) hexagonal arsenic precipitates. Figure 2 and the inset optical diffractogram from the same area of the image reveal the As/GaAs orientation relationship:

$$\{001\}_{\text{As}} \parallel \{1\bar{1}1\}_{\text{GaAs}}$$

$$\langle 100 \rangle_{\text{As}} \parallel \langle 110 \rangle_{\text{GaAs}}$$

It has not been determined whether the basal plane of arsenic is preferentially oriented parallel to either the $\{111\}$ A or $\{111\}$ B planes of GaAs.

As can be seen in Figs. 1-3, images of arsenic precipitates are characterized by strongly contrasting {012} lattice fringes (spacing 0.2771 nm [13], measured spacing 0.275 ± 0.003 nm). This observation is not surprising since the powder diffraction results [13] for x-rays show that the intensity of the 012 reflection is much greater than that of all other reflections. The moiré fringes visible in Fig. 1 (spacing 1.2 nm at $\sim 23^\circ$ from $\langle 001 \rangle$ GaAs toward $\langle \bar{1}10 \rangle$ GaAs) are a result of the interference between the {012} planes of As and the {111} planes of GaAs.

The lattice mismatch between corresponding directions in the basal plane of As and the {111} planes of GaAs is $\sim 6.3\%$. This mismatch results in a structural discontinuity where a larger number of lattice planes in the arsenic phase meet fewer planes from the GaAs phase at their interface. The apparent bending of the lattice planes near the end of the extra {012} arsenic plane in Fig. 3 suggests that extra arsenic planes terminate in interfacial misfit dislocations.

3. Mechanism of oxide growth at 500°C

Thurmond et al [2] have argued that, in terms of bulk free energies, the phases expected during thermal oxidation of GaAs under "weak" conditions are Ga_2O_3 and elemental arsenic. The results presented here are in general agreement with this prediction. Furthermore, any As_2O_3 which might form would be highly volatile [14].

It is well known that arsenic piles up at the interface [15,16]. Wilmsen et al [17] have suggested that the reason for the arsenic

accumulation is that arsenic cannot readily diffuse into the substrate or to the surface through the Ga_2O_3 layer. This view is consistent with the results reported here. However, the decomposition voids suggest that arsenic can escape locally, perhaps through structural imperfections such as cracks or pinholes in the epitaxial Ga_2O_3 film.

The development of the oxide morphology can be described as follows (Fig. 4). In the initial stages of oxidation, Ga_2O_3 , elemental As, and possibly As_2O_3 are formed. Because of the proximity of the As to the surface, the arsenic (and any As_2O_3) is largely evaporated [18]. Although the γ - Ga_2O_3 is epitaxial, there exist structural imperfections (eg. pinholes or cracks) which allow the escape of arsenic in the latter stages of oxidation. Thus, in the vicinity of the cracks or pinholes, the reaction is accelerated (not limited by arsenic accumulation) resulting in the formation of voids at the oxide/GaAs interface. The interfacial regions between the structural imperfections do not contain fast diffusion paths for arsenic, possibly because of the high degree of lattice correspondence between GaAs and γ - Ga_2O_3 . Consequently, as the oxide thickens, arsenic is trapped at the interface in the form of hexagonal precipitates. The observation that the As precipitates protrude into the GaAs substrate (Figs. 1 and 2) suggests that the As precipitates are nucleated by locally high losses of Ga in the GaAs substrate, resulting in the local collapse of the GaAs lattice.

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Figure Captions

Fig. 1(a) Cross-sectional micrograph of the thermal oxide/GaAs interface. Note the large void resulting from oxidation-enhanced decomposition of GaAs. (b) Diffraction pattern from the same area showing the epitaxial nature of γ -Ga₂O₃. (c) High magnification image of the region boxed in (a). The white bar is parallel to the (0 $\bar{1}$ 2) planes of arsenic.

Fig. 2. High magnification image of an arsenic precipitate in GaAs. Confirmation of the orientation relationship (see text) is provided by the optical diffractogram from the same area of the negative.

Fig. 3. High magnification image of the As/GaAs interface showing (0 $\bar{1}$ 2) plane of arsenic terminating in an interfacial misfit dislocation.

Fig. 4. Schematic diagram illustrating the morphological development of the thermal oxide (a) Arsenic which results from oxidation during early stages is sufficiently close to the surface to volatilize. (b) During later stages, significant arsenic loss can occur only through structural imperfections in the thickening γ -Ga₂O₃ film. Arsenic precipitates are nucleated ahead of the oxide/GaAs interface as Ga-depleted regions of the substrate collapse. (c) Final interface morphology consists of voids and arsenic precipitates.

XBB 940-7887

Fig. 1

XBB 840-8018A

Fig. 2

XBB 840-8019

Fig. 3

XBL 8410-4435

Fig. 4

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