MBE grown high-quality Gd_2O_3/Si(111) hetero-structure

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Abstract

A nearly lattice-matched Gd_2O_3/Si(111) hetero-epitaxy was demonstrated using molecular beam epitaxy (MBE). Detailed structural studies find that the nano thick Gd_2O_3 films have a cubic phase with a very uniform thickness, an excellent crystallinity and atomically sharp interfaces. These features are characterized by the bright, streaky reconstructed reflection high-energy electron diffraction (RHEED) patterns at the initial oxide growth, the pronounced interference fringes in the X-ray reflectivity curve as well as in the crystal truncation rod around the substrate diffraction peaks using the high-resolution X-ray diffraction. The (111) axis of the thin oxide is oriented parallel to the substrate (111) normal with a 60° in-plane symmetry rotation.

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1. Introduction

Hetero-epitaxy between insulators and semiconductors is always fascinating scientifically and has gained attention due to its technological application. Many advanced electronic and photonic devices are made of this kind of structures, with a notable example found in the epitaxial growth of GaN on sapphire substrates. However, it is very difficult to achieve a structural perfection in the hetero-epitaxy, due to lattice mismatches and/or vastly different chemical bonding between the over-grown films and the host substrates.

Here, we report growth of Gd_2O_3/Si(111) hetero-structure using molecular beam epitaxy (MBE) and its structural characteristics. The lattice constant of bulk Si, \(a_{\text{Si}}\), and cubic-phase Gd_2O_3 is 5.43 and 10.81 Å, respectively. Doubling the Si unit cell makes a lattice mismatch between them less than 0.5%, perhaps one of the smallest among all the oxides epitaxially grown on semiconductors. Therefore, a nearly lattice-matched oxide/semiconductor heteroepitaxy was expected if Gd_2O_3 is grown with the film normal of (111) parallel to that of the substrate normal. For the growth of Gd_2O_3 on Si(100), epitaxy occurred with the oxide (110), not (100), parallel to the normal of the substrate. Also, there was degeneracy in the oxide in-plane orientation, i.e. existence of two equivalent domains due to an equal possibility of placing two (110)-oriented domains orthogonal to each other. A single-domain growth was achieved on vicinal Si(100) substrates [1]. It was known that the initial growth of oxide on GaAs, electron beam evaporated from a target consisting of single-crystal Gd_3Ga_5O_12 garnet, is a single crystal with a composition of pure Gd_2O_3 [2]. Therefore, the same target was employed to deposit Gd_2O_3 on Si.

Single-crystal oxide films of different thickness deposited on Si(111) wafers were fabricated in a multi-chamber MBE/UHV (ultra-high vacuum) system [3]. Within the studied thickness, the qualitative structural properties of the samples are identical, independent of film thickness. Therefore, in this paper we mainly present the results of a 90 Å thick oxide film. The X-ray reflectivity of the film exhibits pronounced oscillations persisting over 7° in incident angle, \(\theta\), indicating the sharp interfaces. An atomically flat smooth film surface and interface with Si were confirmed using high-resolution transmission electron microscope (HRTEM) imaging.
microscopy (HRTEM). The non-periodic intensity modulation observed in the X-ray reflectivity curve indicates the film is composed of more than a single layer. Gadolinium silicate found at the Gd$_2$O$_3$/Si interface and a thin layer of Ga$_2$O$_3$ at the top surface of the film were observed using an X-ray photoelectron spectroscopy (XPS), which is in situ connected to the multi-chamber MBE/UHV system [4].

2. Experimental procedures

Two inch (111)-oriented Si wafers were RCA-cleaned and HF dipped before being loaded into the multi-chamber system. Sharp streaky (7 × 7) reconstructed surface of chemically clean, atomically ordered Si surface was achieved by heating the substrates to ~680 °C before the oxide deposition. The substrate temperature was maintained at the vicinity of 600 °C. Reflection high-energy electron diffraction (RHEED) was employed to monitor the film growth, particularly at the initial stage.

Measurements of X-ray diffraction were carried out at beamline BL17B of National Synchrotron Radiation Research Center (NSRRC), where X-rays are monochromatized by a pair of Si(111) crystals. Beam energy of 8 keV was employed in most of the measurements. A four-circle diffractometer with two pairs of slits between the sample and detector was employed. A typical resolution of better than 4 × 10^{-4} nm^{-1} is adopted for this work. X-ray reflectivity measurement was conducted using a two-circle diffractometer operated at 50 kV and 200 mA with Cu-K$_{α1}$ radiation (λ = 1.54 Å). By using the modeling fits of BedeREFS Mercury Code, we were able to determine the film thickness, the interfacial roughness and the electron density distribution from the X-ray reflectivity data [5,6].

HRTEM, a JEOL 2100F field-emission TEM operated at 200 kV, was used to reveal the cross-sectional image of the hetero-structure. To probe the composition of the oxide films, in situ XPS analyses were performed [4].

3. Results and discussion

RHEED patterns along the in plane [1 1 1]$_{Si}$ of a sample in initial growth stage (~10 Å thick) and of the as-deposited film (~90 Å thick) were shown in Fig. 1(a) and (b), respectively. The epitaxial oxide film exhibited the same in-plane symmetry as that of the Si(111) substrate. The initial streaky 5 × RHEED pattern indicates a high-quality epitaxial growth of the oxide film. The faint 1 × (compared to the 5 × RHEED pattern) after the oxide growth of ~90 Å thick was probably caused by the surface Ga$_2$O$_3$ layer, as suggested by the X-ray reflectivity and in situ XPS analyses.

X-ray diffraction measurements elucidate that the oxide films were grown epitaxially in a cubic structure, with the (111) axis oriented parallel to the substrate (111) normal. A single-crystal X-ray surface normal scan of the deposited film across Si(111) is shown in Fig. 2, where the abscissa is in units of reciprocal lattice unit (r.l.u.) of Si with the value of 2π/α$_{Si}$. As indicated by the arrow, the broad feature underneath the intense peak from Si(111) substrate is the diffraction peak of Gd$_2$O$_3$ (222). The broadness of the peak is mainly due to the nano-thick nature of the oxide film. Even with the synchrotron radiation, it is difficult to resolve these two peaks due to the very small lattice mismatch. Therefore, no rocking scan along the primary oxide peaks was taken as it is not possible to separate the contribution of the oxide reflection from the tail of intense substrate reflection. The pronounced Pendellosung fringes near the Gd$_2$O$_3$ (222) reflections show a good crystal quality of the epitaxial oxide film and also infer a very uniform film with atomically smooth surface and interface. From the period of the fringes, the oxide thickness contributing to the Gd$_2$O$_3$ (222) diffraction is estimated to be about 67 Å, consisting with the thickness determined using the X-ray reflectivity.

As illustrated in Fig. 3, a pronounced intensity oscillation on the reflectivity curve, which covers eight orders of magnitude, again indicates that the oxide film is highly uniform with atomically smooth interfaces. A modeling fit suggests that the deposited film consists of three layers, from interface to surface: the chemical compositions are gadolinium silicates, Gd$_2$O$_3$, and Ga$_2$O$_3$, respectively, as revealed using the in situ XPS.
The corresponding fitting parameters are shown in Table 1. The overall thickness of the deposited film is about 87 Å while the thickness of gadolinium silicate, Gd$_2$O$_3$, and Ga$_2$O$_3$ layer is 9.01, 63.35 and 15.27 Å, respectively. Note that there is a difference in thickness of 20 Å, estimated from the Pendellosung fringes surrounding the diffraction peak and from the reflectivity curve. The structural difference of the Ga$_2$O$_3$ surface layer and the interfacial silicate layer, which do not contribute to the Gd$_2$O$_3$ (2 2 2) diffraction should be the cause of the discrepancy.

The interfacial roughness at Gd$_x$Si$_y$O/Si substrate, Gd$_2$O$_3$/Gd$_x$Si$_y$O, Ga$_2$O$_3$/Gd$_2$O$_3$ interfaces and surface roughness of Ga$_2$O$_3$ surface layer was estimated, using X-ray reflectivity, to be around 3.07, 2.43, 2.15 and 2.90 Å, respectively.

The full-width at half-maximum of Si{2 2 0} reflections is about 0.0091° and of Gd$_2$O$_3$ {4 4 0} is 0.079°, indicating an excellent in-plane epitaxy. In contrast to a six-fold symmetry of an HCP structure found in the growth of Gd$_2$O$_3$ on sapphire or GaN [8,9], the three-fold symmetry in this work is similar to that of the epitaxial growth of Sc$_2$O$_3$ on Si(1 1 1) [7,10].

Cross-sectional HRTEM micrographs of the heterostructure (not shown) exhibited high quality, uniform images of the film with a very sharp interface. Although compositional distribution along the growth direction was suggested by XPS, there was no observable contrast variation throughout the film, indicating a crystalline silicate with a structure almost identical to that of the Gd$_2$O$_3$ layer. The studies are being carried out to determine
the Si content in the silicate using XPS on oxide films 1 nm thick. The silicate here may have a new crystallographic structure since the known existing silicates such as Gd$_2$SiO$_5$ and Gd$_2$Si$_2$O$_7$ have monoclinic and orthorhombic structures, respectively, vastly different from the cubic phase of Gd$_2$O$_3$.

4. Conclusion

A high-quality single-crystal Gd$_2$O$_3$ film with a structural perfection was epitaxially grown on Si(1 1 1). The interfacial silicate layer, commonly observed in many high-$\kappa$/Si hetero-structures may have a crystallographic structure similar to that of Gd$_2$O$_3$.

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