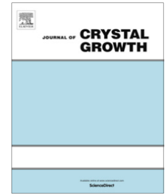
Journal of Crystal Growth 476 (2017) 6–11

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/crys



Epitaxial growth of barium titanate thin films on germanium *via* atomic layer deposition

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ARTICLE INFO

Article history:
Received 15 April 2017
Received in revised form 4 August 2017
Accepted 5 August 2017
Available online 7 August 2017
Communicated by T.F. Kuech

Keywords:
A1. Interfaces
A3. Atomic layer deposition
B1. Perovskites
B2. Ferroelectric materials

ABSTRACT

Barium titanate $BaTiO_3$ (BTO) thin films were epitaxially grown at 225 °C on 2 × 1-reconstructed Ge(001) surfaces *via* atomic layer deposition (ALD). Approximately 2 nm of BTO film was grown directly on Ge(001) as an amorphous film. Electron diffraction confirmed the epitaxy of the BTO films after post-deposition annealing at 650 °C. Additional BTO layers grown on the crystalline BTO/Ge(001) film were crystalline as-deposited. X-ray diffraction indicated that the epitaxial BTO films had a *c*-axis out-of-plane orientation, and the abrupt BTO/Ge interface was preserved with no sign of any interfacial germanium oxide. Scanning transmission electron microscopy provided evidence of Ba atoms occupying the troughs of the dimer rows of the 2 × 1-reconstructed Ge(001) surface, as well as preservation of the 2 × 1-reconstructed Ge(001) surface. This study presents a low-temperature process to fabricate BTO/Ge heterostructures.

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1. Introduction

The epitaxial integration of perovskite metal oxides on silicon, first reported by McKee et al. [1], demonstrated the promise of using epitaxial metal oxides in semiconductor applications [2]. Numerous researchers have subsequently demonstrated the epitaxial growth of different perovskite oxides on Si(001) and Ge(001), such as $SrTiO_3$ (STO), $BaTiO_3$ (BTO), $PbZr_xTi_{1-x}O_3$, $SrHfO_3$ (SHO), $SrHf_xTi_{1-x}O_3$, $LaCoO_3$, and $LaAlO_3$ [1,3–16]. Integration of perovskites oxides with semiconductor materials potentially allows new device structures that combine their wide range of oxide properties, including high permittivity, ferromagnetism, electro-optic effect, and ferroelectricity, with logic applications [6,8–10,12,14,16–18]. Ge provides higher hole and electron mobilities compared with Si [19,20], which can enable faster device operation. As a result, there is increased interest in using Ge as a channel material in field effect transistor (FET) fabrication. In applications such as high-*k* dielectrics, it is undesirable to have an additional oxide layer that will lower the effective capacitance of the eventual transistor structure as GeO_2 permittivity is only about 6. The GeO_2 native oxide formed on Ge surface is relatively unstable, and can be thermally removed by vacuum annealing prior to growth [5,21]. Ability to remove Ge native oxide enables opportunities to fabricate perovskite-Ge heterostructures without formation of a low-permittivity, amorphous GeO_x layer at the oxide-Ge interface.

The perovskite BTO is of interest due to its ferroelectricity and high permittivity [6,7,10,18,22,23]. The ferroelectricity of BTO enables the possibility of devices such as ferroelectric FETs [24,25], negative-capacitance devices [10,18,24–27], and may have applications in nanophotonics [8,17,28,29]. Device structures integrating BTO with Si and Ge have been demonstrated using pulsed laser deposition [30], chemical vapor deposition [31], and molecular beam epitaxy (MBE) [8,10,14,18,32,33].

MBE has been the primary method used for growing high quality epitaxial BTO films due to its layer-by-layer growth mode and precise control of oxygen pressure [34]. However, atomic layer deposition (ALD) provides several advantages for oxide growth. ALD allows for low temperature processing, scalability, and conformal coverage, which are desirable in an industrial setting [35,36]. Although various perovskite films, including STO, BTO, and $LaAlO_3$, have been epitaxially integrated to Si using ALD, an initial STO

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http://dx.doi.org/10.1016/j.jcrysgro.2017.08.003
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template layer grown by MBE is necessary to prevent formation of a SiO_x layer during ALD growth [6,13,37–39].

It has recently been demonstrated that ABO_3 perovskite films, such as STO, SHO, and $SrHf_xTi_{1-x}O_3$, can be epitaxially grown onto Ge(001) surfaces *via* ALD without using the STO template [5,9,11]. The ALD of STO and SHO on Ge(001) utilized a two-step process for film thicknesses greater than 2 nm and 5 nm, respectively [5,9]. For STO, an initial 2-nm layer was deposited as an amorphous film and annealed to become crystalline, and then additional STO was deposited [5]. Both STO and SHO growth required deposition of a compositionally Sr-rich film as the first step. In the case of STO, a Sr-rich cycling ratio of 2:1 strontium bis(triisopropylcyclopentadienyl):titanium isopropoxide was used for the initial layer and then a 4:3 cycle ratio was used for the subsequent layers [5].

The deposition of barium bis(triisopropylcyclopentadienyl) on reconstructed Ge(001) surfaces has been shown to produce a $BaGe_x$ Zintl-like layer, which is akin to the $BaGe_x$ layer formed by depositing Ba on Ge *via* MBE [40]. Barium bis(triisopropylcyclopentadienyl) will dissociate upon adsorption onto the Ge(001) surface, as opposed to undergoing the ligand exchange mechanisms with surface adsorbates in a typical metal-oxide ALD process [35,41]. Simulation results also suggest a path to Sr deposition on TiO_2-terminated STO without ligand exchange by using precursors with cyclopentadienyl ligands [42]. Herein we report a two-step process to grow epitaxial BTO films on Ge(001) that first involves growth, and crystallization through annealing, of a 2-nm amorphous BTO layer on which additional crystalline BTO is grown. The presence of a Zintl-like $BaGe_x$ layer at the BTO-Ge (001) interface is also observed.

2. Experimental

The procedure used to deposit BTO thin films on Ge is analogous to that used for STO on Ge [5]. The as-received 4-inch Ge(001) wafer (Sb-doped, from MTI Corp.) is diced into $16 \times 20\ mm^2$ rectangles. The diced Ge samples are degreased in ultrasonic baths of acetone, isopropyl alcohol, and then deionized water, for 10 min each. The sample is then dried with high purity nitrogen and placed under an ultraviolet/ozone cleaner (Novascan PSD-UY6 and PSD-UV OES-1000D) for 30 min to remove residual carbon contamination. The cleaned sample is then immediately introduced into the load lock of the vacuum system and pumped to a vacuum level below 5×10^{-7} Torr using a turbomolecular pump. The vacuum system consists of an MBE system, an ALD reactor, and an analytical chamber connected to a vacuum transfer line. The sample is then annealed in vacuum (<2.0×10^{-8} Torr) at 700 °C for 1 h to remove surface GeO_2. Reflection high-energy electron diffraction (RHEED) is used to monitor sample deoxidation, which is indicated by observation of a 2×1-reconstructed Ge(001) surface. The deoxidized Ge(001) sample is then cooled down to 200 °C and transferred *in vacuo* into the ALD chamber.

The ALD reactor used in this study is a custom-built, cross-flow type reactor; a detailed description is given elsewhere [37,38]. Briefly, the hot-wall stainless steel reactor is kept at a base pressure below 1×10^{-6} Torr using a turbomolecular pump. Continuously-flowing Ar is used as both the carrier and purging gas for the reactor, giving a reactor pressure of approximately 1 Torr during ALD. Barium bis(triisopropylcyclopentadienyl) [Ba $(^iPr_3Cp)_2$] (Hyper-Ba, supplied by Air Liquide) and titanium tetraisopropoxide (TTIP, supplied by Sigma-Aldrich) were used as the precursors for Ba and Ti, respectively. The reactor is set to 225 °C before introducing the substrate, while Hyper-Ba is heated to 148 ± 3 °C and TTIP to 37 ± 2 °C. After loading the substrate into the ALD chamber, the substrate is left for at least 20 min to allow thermal equilibrium between the substrate and the reactor to be reached. A deposition consisting of 28 ALD unit cycles with 4:3 Ba:Ti cycling ratio is used to deposit ~2-nm amorphous BTO on Ge. A unit cycle consists of a 2-s precursor (Hyper-Ba or TTIP) dose, followed by a 20-s Ar purge; and then a 1-s co-reactant dose followed by a 20-s Ar purge. Water is used as the co-reactant for both Ba and Ti ALD unit cycles. The amorphous BTO films grown on Ge are crystallized by annealing the sample in vacuum (<2.0×10^{-8} Torr) without the presence of oxygen at 650 °C for 5 min, with the temperature ramp rate no greater than 10 °C/min. RHEED is used to check for crystallinity of the BTO films after vacuum annealing. Once crystallinity is confirmed, additional BTO is grown using the same procedure, with the exception of using a 4:5 Ba:Ti cycling ratio rather than 4:3.

Throughout the growth and annealing process, the sample is transferred *in vacuo* to the analytical chamber, which is equipped with an X-ray photoelectron spectrometer for composition and oxidation state measurement. X-ray photoelectron spectroscopy (XPS) is performed using a VG Scienta R3000 analyzer and a monochromated Al K-α source at 1486.6 eV. The analyzer is calibrated using a silver foil, where the Ag $3d_{5/2}$ core level is defined to be 368.27 eV and the Fermi level of Ag at 0.00 eV. Film compositions are estimated by using CasaXPS (Version 2.3.16), with Shirley background subtraction and relevant sensitivity factors for peak fitting of each element. Sensitivity factors were obtained by both using Handbook of X-ray Photoelectron Spectroscopy [43] and calibration using a BTO crystal.

X-ray diffraction (XRD) is used *ex situ* to evaluate the crystal structure of the grown BTO films, while X-ray reflectivity (XRR) is used to measure the film thickness. Both XRD and XRR are performed using a Rigaku Ultima IV X-ray diffractometer with thin film attachments. The diffractometer uses the Cu K-α emission line as the X-ray source. The ALD-grown BTO film and BTO/Ge interfaces were further examined by high-angle annular-dark-field scanning transmission electron microscopy (HAADF-STEM). The samples were prepared *via* standard cross-section method with Ar-ion-milling. The aberration-corrected STEM images were taken with a JEOL ARM-200F operated at 200 kV. The beam convergence angle was set to 20 mrad, and the HAADF images were recorded with a collection angle of 90–150 mrad.

3. Results and discussion

After the deoxidation step, RHEED was used to confirm the 2×1 surface reconstruction. The RHEED pattern of a cleaned, deoxidized Ge(001) surface is shown in Fig. 1(a). The initial 2-nm BTO film deposited on the 2×1-reconstructed Ge(001) surface was amorphous as-deposited. Fig. 1(b) shows the RHEED pattern after the initial 2-nm BTO deposition; the absence of diffraction features confirms the film to be amorphous. The amorphous BTO film crystallizes after 5 min of vacuum annealing at 650 °C, as shown in Fig. 1(c). The RHEED pattern for the BTO film after annealing *in vacuo* appeared to be crystalline with square symmetry and having a single in-plane epitaxial orientation.

According to XPS measurements, we observe crystallization of the BTO template layer with the Ba/Ti ratio between 0.92 and 1.30. The Ba/Ti ratio range differs from the ideal ratio of unity for ABO_3 perovskites. However, with formation of a $BaGe_x$ Zintl-like layer, the BTO/Ge structure is expected to have more Ba than Ti. In an ideal scenario, there would be a half-monolayer of Ba between the BTO and Ge layers due to the Zintl-like layer. Assuming that this ideal BTO template layer has a uniform thickness of 5 unit cells (~2 nm), the BTO/Ge structure would have 5.5 monolayers of Ba atoms and 5 monolayers of Ti atoms deposited on the Ge(001) surface, yielding a Ba/Ti atomic ratio of 1.10. In practice, the BTO template layers on Ge(001) can crystallize as long as the

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