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Germanium films with strong in-plane and out-of-plane texture on flexible, randomly textured metal substrates

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Abstract

High efficiencies have been achieved in photovoltaic cells based on III–V compounds grown on single crystal germanium substrates. Since the size of these substrates is limited and their cost is very high, such III–V photovoltaics have not found widespread terrestrial use. The objective of this work is to develop highly textured, epitaxial germanium thin films on inexpensive substrates suitable for roll-to-roll continuous processing to serve as templates for III–V compounds. Germanium films with a high degree of in-plane and out-of-plane texture have been demonstrated on randomly textured, flexible nickel alloy substrates by epitaxial growth on template films made by ion beam-assisted deposition (IBAD). In order to achieve epitaxial growth, an intermediate layer of CeO₂ was found to be required between the IBAD MgO template and the Ge film. Our study shows that structural match between Ge and the underlying oxide layer is the key to epitaxial growth. Room temperature optical bandgap of the Ge films was identified at 0.67 eV suggesting minimal residual strain in the film. Refraction index and extinction coefficient values of the epitaxial Ge film were found to match well with that measured from a reference Ge single crystal.

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1. Introduction

Due to their excellent lattice and structural match with GaAs, Ge is commonly used as substrates for III–V semiconductor films for various applications such as photovoltaics and optoelectronics. Photovoltaic cells based on III–V compounds have exhibited efficiencies of about 40%, but have found only limited use because of their cost, which is primarily driven by the high cost of single crystal Ge substrates. Additionally, multi-junction or tandem cells which have resulted in high efficiencies in III–V compounds have been viable only with single-crystalline individual cells [1]. At the other end of the spectrum, thin film solar cells offer the advantage of low-cost fabrication, but have not yielded the higher efficiencies of single-crystalline cells. Misfit dislocations at high-angle grain boundaries have been identified as traps to charge carriers reducing the open circuit voltage of polycrystalline solar cells [2]. If highly textured, epitaxial Ge films could be achieved on polycrystalline, flexible substrates, then roll-to-roll processing of inexpensive ultra-high efficient III–V thin film photovoltaics could be enabled. The enabler that we have employed to achieve such an architecture is a biaxially-textured template made by ion beam-assisted deposition (IBAD) [3,4]. In the IBAD process, materials with rock-salt structures such as MgO are deposited on amorphous layers on polycrystalline substrates, with simultaneous ion beam bombardment. Under appropriate conditions, within a first few nanometers of the film, a good degree of biaxial texture is achieved. Such biaxially-textured films have been successfully employed as templates for epitaxial growth of cube-textured superconducting films on polycrystalline substrates with critical current densities as high as those achieved on single crystal substrates [5,6]. In fact, kilometer lengths of IBAD-based templates are routinely produced with in-plane texture of about 6° full-width-at-half-maximum (FWHM) [6].

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0022-0248/ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2009.08.030
this study, we adopted the IBAD technique to synthesize highly textured, epitaxial germanium films that can then be used for high quality III–V semiconducting photovoltaic films such as GaAs. While IBAD templates have been used for Si growth [7], we are not aware of any work on epitaxial Ge on these templates on flexible substrates. Recombination of charge carriers at grain boundaries and other defects has been determined to be a primary loss mechanism in silicon cells [2]. Hence, there have been efforts to minimize grain boundaries in silicon by crystallization of amorphous silicon films on large-grained templates [8] or epitaxially grow them on biaxially-textured, large-grained metal substrates [9]. Similar work on III–V semiconducting photovoltaic films has not been conducted partly because of the unavailability of suitable substrates. The present study provides an opportunity to evaluate the potential benefit of III–V photovoltaic film growth on highly-textured Ge films with only small-angle grain boundaries.

2. IBAD templates

All films in the multilayer architectures prepared in this study were grown in reel-to-reel thin film deposition systems. Fig. 1 is a schematic of the architecture that was developed in this work. Hastelloy C-276 substrates, 12 mm in width and 50 μm in thickness were electropolished to a surface roughness better than 1 nm as measured by atomic force microscopy. An 80 nm thick Al₂O₃ film and a 7 nm thick Y₂O₃ film were deposited at room temperature by reactive magnetron sputtering using metal targets on the polished Hastelloy substrates. The alumina layer serves as a diffusion barrier to cations from the substrate that could otherwise poison the electrically active layers. In comparison to other materials, only a thin layer of alumina is needed to be an effective diffusion barrier which is desirable for high-throughput manufacturing. The yttria layer provides a pristine surface for nucleation of the IBAD film. Biaxial texture development during IBAD of MgO occurs during the nucleation stage within the first few nanometers and hence it can be compromised by the templating effect if the IBAD film is grown on a polycrystalline surface. When grown on amorphous or nanocrystalline surfaces, any kind of the templating effect on IBAD MgO is avoided. IBAD films were made by ion beam sputtering of MgO at room temperature with simultaneous bombardment of the substrate with an Ar ion beam inclined at 45° to the substrate normal. A beam voltage of 900 eV and beam current of 180 mA were used. Reflection high energy electron diffraction (RHEED) was used in situ during IBAD to confirm and qualify the texture development in the growing MgO film. Homo-epitaxial MgO, about 30–50 nm in thickness was grown on the IBAD films by reactive magnetron sputtering of Mg at a temperature of 700–750 °C. X-ray diffraction (XRD) measurements on the homo-epitaxial MgO film showed an in-plane texture of 6–7° FWHM.

3. Epitaxial germanium

All Ge films reported in this work were deposited using the following conditions except for deposition temperature variations. A 50 nm thick Ge was grown using a reel-to-reel r.f. magnetron sputtering system using Ge targets. The deposition was conducted at 250 W at a pressure of 4 mTorr in an atmosphere of Ar–4% H₂ (4% H₂ with remainder Ar) at a tape moving speed of 2 cm/min. First, the homo-epitaxial MgO films were used as template to grow Ge films. Six samples were fabricated at deposition temperatures of 600, 650, 720, 770, 820 and 850 °C all in a single run without venting the system. Reel-to-reel systems provide this benefit of multiple deposition conditions in a single run by which unintended variations from run to run can be avoided as well as exploration of a large range of process parameters can be expedited. Theta–2theta XRD measurements conducted on all samples showed polycrystalline Ge films with all major crystallographic orientations. Also, the desired (400) peak of Ge was found to be weak in all samples. Fig. 2 exhibits a theta–2theta pattern obtained from a Ge film grown on MgO at 600 °C showing intense (220) and weaker (111), (400) and (311) Ge peaks. It was clear that epitaxial growth of Ge was not possible directly on MgO. The lattice parameter of MgO is 4.22 Å and that of Ge is 5.646 Å. The edge-on-edge lattice mismatch between the two materials is quite high ~33.8%. However, we expect, based on extensive experience with heteroepitaxial growth of various materials on IBAD templates [10–13], that Ge could grow rotated by 45° within the film plane, i.e. [100] direction of Ge matching with [110] direction of MgO. In such an instance, the lattice mismatch can be substantially reduced. However, even with this rotation, there would exist a large lattice mismatch between MgO and Ge (5.4%).

Next, in order to minimize the lattice mismatch, we deposited an intermediate layer of epitaxial LaMnO₃ on the homo-epitaxial MgO film. LaMnO₃ has been previously successfully employed as a cap layer on IBAD MgO-based templates for growth of high performance oxide superconducting films [5,6,11]. Further, the lattice parameters in the basal plane of LaMnO₃ are a=5.53 Å and b=5.71 Å which results in lattice mismatch with Ge of ~2.1% and 1.1% respectively, much better than in the case of MgO. Additionally, it was expected that edge-on-edge epitaxy of Ge, without 45° rotation should be possible. LaMnO₃ was deposited by r.f. sputtering of about 30–50 nm in thickness was grown on the homo-epitaxial MgO on IBAD MgO at a temperature of 700–750 °C. XRD measurements on the LaMnO₃ films confirmed heteroepitaxial growth with an in-plane texture of 6–7° FWHM.

Ge films of identical thickness of about 50 nm were then deposited on five LaMnO₃ buffered IBAD tapes at deposition temperatures of 500, 530, 550, 580, and 650 °C. XRD theta–2theta pattern obtained from a Ge film deposited at 580 °C on LaMnO₃ on IBAD template is shown in Fig. 2. This film as well as those grown at other temperatures showed signs of polycrystalline Ge growth. (111) and (311) peaks of Ge are clearly evident in addition to a weak (400) peak. The fact that even with a much improved lattice

Fig. 1. (color web only) Schematic of the multilayer architecture developed in this work on growth of biaxially-textured Ge films on IBAD templates.
match, Ge did not grow epitaxially on LaMnO$_3$ indicated that there should be other factors key for epitaxial growth of Ge using IBAD templates such as structural and chemical incompatibilities. Chemical incompatibility could be due to the formation of an intermediate phase between LaMnO$_3$ and Ge although no such information has been found in the literature. We have successfully grown non-oxides such as Ni epitaxially on LaMnO$_3$ as well as on MgO using IBAD templates and it is not obvious why there would be a chemical compatibility issue in the growth of Ge on LaMnO$_3$ or on MgO. Structural incompatibility could be due to the lack of match of the atomic locations of the basal plane of Ge and LaMnO$_3$. Ge has a diamond structure with atoms in the four tetrahedral hole locations, projections of which on the basal plane are at $\frac{1}{4}$,$\frac{3}{4}$,$\frac{1}{2}$,$\frac{1}{2}$. 0 and $\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{2}$,$\frac{1}{2}$. LaMnO$_3$ and MgO possess a perovskite structure and rock-salt structure respectively with no atoms in the tetrahedral holes and hence do not have a good structural match with Ge.

We then focused specifically on the issue of structural compatibility between Ge and the underlying oxide layer. In this regards, we investigated an alternate layer, CeO$_2$, between Ge and IBAD MgO. The lattice parameter of CeO$_2$ is 5.41 Å which results in a high mismatch of ~4.5% with Ge, almost as high as that between MgO and Ge (considering 45° rotation of Ge lattice on MgO). We still chose CeO$_2$ because of its better structural match with Ge. CeO$_2$ has a fluorite structure with atoms in the eight tetrahedral hole locations, projections of which on the basal plane are at $\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{4}$, 0,$\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{4}$, 0 and $\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{4}$. 0. LaMnO$_3$ and MgO possess a perovskite structure and rock-salt structure respectively with no atoms in the tetrahedral holes and hence do not have a good structural match with Ge.

Ge was then deposited on six CeO$_2$ buffered IBAD tapes at deposition temperatures of 500, 550, 580, 600, 640, 670, and 720 °C. XRD theta–2theta pattern obtained from a Ge film deposited at 600°C on CeO$_2$ template is shown in Fig. 2. The presence of an intense single orientation of CeO$_2$ (200) is obvious in the figure. Also, a strong Ge (400) orientation is seen, much stronger than the (400) peaks observed in Ge films grown directly on MgO and LaMnO$_3$. No evidence of (111) or other peaks of Ge is present indicating the preferential out-of-plane texture of (400) in the Ge film. The insets in Fig. 2 show the clear absence of (111) and (311) peaks of Ge compared with the films grown on MgO and LaMnO$_3$.

Fig. 2 displays theta–2theta XRD patterns obtained from Ge films deposited over a temperature range 500–720°C focusing in the angular range of the Ge (400) peak. It is seen from the figure that the most intense Ge (400) peak occurs in the samples deposited at 580 and 600°C. The Ge (400) peak intensity is diminished at lower and higher deposition temperatures. Interestingly, even though the same CeO$_2$ film was used for growth of all six samples of Ge, it can be seen from Fig. 2 that the CeO$_2$ (400) peak intensity itself becomes weaker at higher temperatures. It is possible that the ceria layer is modified by the reducing atmosphere used in the deposition of Ge at higher deposition temperatures. If that is the case, then a proper template will not be available for epitaxial Ge growth which could explain the weaker Ge peaks at higher deposition temperatures.
The in-plane texture of Ge was measured by XRD (111) polefigure measurements of Ge and data are shown in Fig. 4. A clear four-fold symmetry is shown in the figure without the presence of other orientations. This result clearly demonstrates strong biaxial texture achieved in Ge epitaxially grown on CeO$_2$ on IBAD MgO template on metal substrate. The spread in the in-plane texture of Ge is calculated to be 6.6$^\circ$FWHM which is comparable to that of the underlying IBAD MgO template. Based on our work on superconducting oxide films on IBAD templates, we expect that this texture can be sharpened with growth of thicker heteroepitaxial layers.

High-resolution X-ray diffraction data were obtained from the (004) peak of Ge film and data is shown in Fig. 5. The peak is found to be sharp at 2800 arcsec indicating the strong texture and crystallinity of the film. The width of the peak indicates a defect density in the range $10^8$–$10^9$ cm$^{-2}$ which needs to be improved for device quality III–V semiconductor growth.

Surface roughness and topography examination of the Ge films grown at various temperatures on CeO$_2$ on IBAD template was conducted using atomic force microscopy (AFM) and scanning electron microscopy (SEM). Results from a Ge film deposited at 600$^\circ$C are shown in Fig. 6. The RMS surface roughness of the film is found to be about 9 nm which is similar to that measured on Ge grown at lower temperatures. But, this value is significantly higher than the surface roughness of 2–3 nm measured in the CeO$_2$ layer. Further, the surface roughness was found to increase to about 17 nm in Ge films grown at higher temperatures. So, 600$^\circ$C is an optimum deposition temperature from the viewpoint of sharpness of texture and film smoothness. As seen in Fig. 6, the grain size of Ge film grown at 600$^\circ$C is about 200 nm. This value is comparable to the grain size of the IBAD MgO film deposited at room temperature and indicates that no significant grain growth occurred in subsequent deposition of epitaxial layers at high temperature.

### 4. Optical properties

The optical properties of biaxially-textured Ge films were further verified by photoreflectance and ellipsometry measurements. The photoreflectance analysis revealed that the position of indirect (L minima) bandgaps positions of the Ge films at $\sim$0.67 eV which is nearly identical to that of bulk-like Ge, suggesting minimal lattice mismatch strain in the film. Spectroscopic ellipsometry (SE) analyses were performed using a Wollam M2000D rotating compensator ellipsometer. In order to reduce correlation between the variables, $\Psi$ and $\Delta$ data were collected at multiple incident angles 40$^\circ$, 50$^\circ$, 60$^\circ$ and 70$^\circ$. Excellent fitting of the measured SE data was accomplished using typical parameterized oscillator functions to obtain Kramers–Kroenig consistent optical parameters of the Ge layer. Data obtained for the evolution of the refraction index and extinction coefficient measurement as a function of the incident photon energy are shown for the Ge film on IBAD template in Figs. 7 and 8 respectively. It can be seen from both figures that the refraction index and extinction coefficient values of the Ge film grown on IBAD template match well with that from a reference bulk Ge single crystal. This information
further corroborates the single-crystalline-like nature and the high optical quality of the Ge film grown on IBAD template on polycrystalline substrate.

Additional experiments have further confirmed the strong crystalline quality of Ge films prepared in this work and will be described in a separate publication [14]. RHEED patterns obtained from the film exhibited c(2 × 2) (mixed (2 × 1)–(1 × 2)) surface reconstruction, typical of high-end homo-epitaxial growth of Ge (1 0 0). Furthermore, epitaxial (1 0 0) GaAs has also been successfully grown by molecular beam epitaxy (MBE) on the Ge films on polycrystalline substrate and strong photoluminescence signal and good optoelectronic properties have been obtained [14]. The ability to grow epitaxial Ge films with excellent out-of-plane and in-plane texture on flexible polycrystalline substrates by reel-to-reel tape processing now provides an immense potential to fabricate high quality III–V semiconductors on long-length/large-area flexible, inexpensive substrates.

5. Conclusions

MgO templates made by ion beam-assisted deposition on flexible metal substrate have been successfully used for epitaxial growth of germanium films. Ge was not found to grow epitaxially directly on MgO. Epitaxy of Ge was not possible even on LaMnO₃ that was epitaxially grown on MgO even though the lattice mismatch between Ge and LaMnO₃ is about 1–2%. In spite of a 4.5% lattice mismatch, excellent heteroepitaxial growth of Ge was achieved on CeO₂ that was in turn grown on LaMnO₃ on IBAD MgO template on metal substrate. This result is believed to be due to the good structural match between diamond Ge and fluorite CeO₂, both of which contain atoms in the same four tetrahedral hole locations. Rock-salt MgO and perovskite LaMnO₃ do not have atoms in the tetrahedral hole locations and hence do not have a good structural match with Ge. Chemical compatibility issue may also be a factor and needs to be further examined. The strongest Ge (4 0 0) out-of-plane texture was achieved in the deposition temperature range 580–600 °C. XRD polefigure measurements showed a good in-plane texture value of 6.6° FWHM in the epitaxial Ge film. Room temperature optical bandgap of the Ge films measured by photoreflectance was identified at 0.67 eV indicating minimal residual strain in the film. Refraction index and extinction coefficient values of the epitaxial Ge film measured by ellipsometry were found to match well with that measured from a reference Ge single crystal.

References