Small angle grain boundary Ge films on biaxial CaF$_2$/glass substrate

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**Abstract**

We demonstrated that it is possible to grow single crystal-like Ge films on a glass substrate using a biaxially textured CaF$_2$ buffer layer at a low temperature of $\sim$400 °C. The CaF$_2$ buffer layer with the (1 1 1) orientation was grown by the oblique angle deposition technique and characterized by X-ray pole figure analysis. Transmission electron microscopy revealed that the Ge(1 1 1) heteroepitaxial films possess a single crystal-like structure with small angle grain boundaries of $\leq$2° misorientation.

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**1. Introduction**

The use of biaxially textured semiconductor film as a substitute for single crystal film has drawn considerable attention because it approximates the properties of single crystal film while providing a downstream cost benefit, especially on large area electronics applications such as displays and photovoltaic devices [1–3]. In a biaxially textured film, the crystallographic orientations of the adjacent grains are closely aligned and the effect of the grain boundaries on carrier scattering is reduced [1]. While a direct growth of semiconductor on an amorphous substrate such as glass results in either polycrystalline or fiber textured film, biaxially textured films of insulating materials such as MgO (through ion beam assisted deposition) and CaF$_2$ (through oblique angle deposition) have been successfully grown on amorphous substrates [4,5]. Biaxial MgO buffer layers have been used to grow small angle grain boundary high $T_c$ superconductor films that can achieve a high critical current [6,7]. High $T_c$ superconductor tapes are now commercially available. CdTe semiconductor has been grown heteroepitaxially on biaxial CaF$_2$ buffer layers on glass [8]. In this article we report a heteroepitaxial growth of biaxially textured Ge film on glass substrate with biaxially textured CaF$_2$ as a buffer layer.

**2. Experimental details**

A biaxially textured CaF$_2$ film was first deposited on Corning 2947 glass substrates (Corning Inc., Corning, NY) by oblique angle vapor deposition technique with a deposition angle of 65° with respect to the surface normal. This film consisted of $\sim$900 nm tall vertically aligned nanorods. Then this film was capped by $\sim$200 nm thick CaF$_2$ layer deposited under normal vapor incidence. The details of this deposition procedure have been described elsewhere [5]. Germanium films were simultaneously deposited by thermal evaporation on unbuffered (bare glass) and CaF$_2$ buffered glass substrates with substrate temperatures of 200, 250, 300, 350 and 400 °C. The substrate temperatures were determined by a K-type thermocouple placed on the substrate surface receiving the incident vapor flux. All the Ge depositions were carried out in a high vacuum chamber with a base pressure of $5 \times 10^{-8}$ Torr. The substrate to source distance was $\sim$30 cm and the pressure during deposition was $\sim$8 $\times 10^{-4}$ Torr. The normal deposition rate for the Ge was $\sim$10 nm/min. The deposition rate and film thicknesses were monitored by a quartz crystal microbalance (QCM) and were verified through cross-section SEM images (Carl Zeiss Supra SEM 1550). The crystallography and texture of the films were studied through XRD and X-ray pole figure analysis using Bruker D8 Discover Diffractometer with Cu target (wavelength=0.15405 nm). The microstructure and the epitaxy properties of Ge on CaF$_2$ were characterized by TEM (model JEOL 2010, 200 kV).

**3. Results and discussion**

Figs. 1(a) and (b) show the plan and cross-sectional view of the scanning electron microscope (SEM) images of the Ge/CaF$_2$/Glass samples grown at a substrate temperature of 400 °C. The plan view image shows that the Ge film is rough with sizes of the
surface asperities on the order of 50–200 nm. The cross-sectional view of the image shows an approximately 600 nm thick Ge film grown on the CaF$_2$ buffered glass substrate.

Fig. 2(a) shows the X-ray diffraction (XRD) line profiles of the Ge films grown simultaneously on glass (bottom curve) and on CaF$_2$/glass (top curve) at a substrate temperature of 400 °C. A comparison of these line profiles with a Ge powder diffraction pattern shows that the Ge film grown on CaF$_2$/glass is highly oriented with the (1 1 1) as the out-of-plane direction. The Ge film grown on glass however was polycrystalline (with a slight preference for the (1 1 1) texture). The (1 1 1) peaks of the XRD line profiles for Ge/CaF$_2$/Glass samples grown at various temperatures are shown in Fig. 2(b). The CaF$_2$ buffer layer used in this work had a (1 1 1) < 1 2 1 > biaxial texture orientation as discussed in reference [5]. In our work, the Ge films were either amorphous (at 200 and 250 °C growth temperature) or had the (1 1 1) < 1 2 1 > biaxial orientation (300 °C or above) similar to that of CaF$_2$ buffer layer. At temperatures 300 °C or above, both Ge(1 1 1) and CaF$_2$(1 1 1) peaks are visible. A closer inspection of the peak intensities reveal the highly textured nature of the Ge films grown at 300 °C or higher temperature. While the full-width at half-maximum (FWHM) of the CaF$_2$(1 1 1) peak is unchanged, the FWHM of Ge(1 1 1) peak decreases as the growth temperature increases. This trend holds up to the highest temperature (400 °C) used in this study.

Figs. 3(a) and (b) show the CaF$_2$(1 1 1) and Ge(1 1 1) pole figures taken from the Ge/CaF$_2$/Glass sample grown at 400 °C. These pole figures are similar to the theoretical (1 1 1) poles projected along the [1 1 1] direction of a cubic crystal with the [1 1 1] direction tilted off the substrate normal by −11°.

Therefore, an approximate out-of-plane orientation of both the CaF$_2$ buffer layer and the Ge film is the [1 1 1] direction. The dispersions in the [1 1 1] orientation of the CaF$_2$ and Ge films were approximately ±5° and ±3°, respectively. The in-plane orientation of the CaF$_2$ buffer layer was determined based on the X-ray pole figure, transmission electron microscopy (TEM) images and the geometry of the CaF$_2$ nanorods as discussed elsewhere [5]. The CaF$_2$ did not exhibit any poles corresponding to growth twins. The (1 1 1) pole figure of Ge shows two kinds of poles. The intensities of poles that have the same orientation of CaF$_2$ (labelled by (1 T 1), (1 1 T) and (T 1 1)) are about 1/5th the intensity of poles rotated by 180° (labelled B(1 1 1), B(1 1 T) and BT(1 1 1)) about the [1 1 1] direction of CaF$_2$. It should be noted that the poles indicated by B(1 1 T), B(1 1 T) and BT(1 1 1) can be either from the growth twins of the type A epitaxial film where the film orientation is same as the substrate or from a type B epitaxial film where the Ge over-layer grew 180° rotated about the [1 1 1] direction of the CaF$_2$ film. However, the extremely high intensity of the 180° rotated poles suggests that type B epitaxy was preferential in the growth of Ge on CaF$_2$. In Fig. 3(b), the pole positions labelled a, b and c are the result of twinning about B(1 T 1), B(1 1 T) and BT(1 1 1) positions, respectively.

The epitaxial growth temperature for Ge on CaF$_2$ has been quoted to be from around 300 to 700 °C for Ge on CaF$_2$[9–13]. In our work, the Ge film was either amorphous at 200 and 250 °C growth temperature or had the (1 1 1) < 1 2 1 > biaxial orientation at 300 °C or above. The Ge films grown at temperatures of...
300, 350 and 400 °C were all biaxially textured, where the sample grown at 400 °C had the best crystalline quality. This can be inferred from the FWHMs of the Ge(1 1 1) peaks shown in Fig. 2(b). In addition, the biaxially textured Ge film grown at 400 °C had low angle grain boundaries verified from transmission electron microscopy images and is presented next.

Fig. 4(a) shows the cross-section TEM image of the Ge film on CaF2 buffered glass substrate. There is a high density of twinning, stacking faults and dislocations in the Ge layer. Columnar grain structure was not observed over the analyzed region (a few microns). Figs. 4(b), (c) and (d) show the selected area TEM diffraction patterns taken from the Ge layer, the Ge/CaF2 interfacial region and CaF2 layer, respectively. The spots circled in the diffraction patterns in Figs. 4(b) and (c) are from Ge that overlap with CaF2 diffraction spots indexed in Fig. 4(d). In addition to these, more diffraction spots are observed from the Ge layer due to twinning. These twin diffraction spots about mirror vector $m_1$ are labelled $T_1$ and $T_2$ in Fig. 4(b). In Fig. 4(b), the twin diffraction spots of (1 1 1) and (1 1 1 T) and those of (0 2 0) and (0 2 0) about mirror vector $m_1$ are labelled $T_1$ and $T_2$, respectively. The twin diffraction spots of (1 1 1) and (TTT) about mirror vector $m_2$ are labelled $T_3$. Note that the labels $T_1$ and $T_3$ in Fig. 4(b) correspond to label B in Fig. 3(b). The other weaker diffraction spots in Fig. 4(b) are from secondary twinning of diffraction spots labelled $T_1$, $T_2$ and $T_3$. The secondary twins of diffraction spots labelled $T_1$ and $T_2$ correspond to the labels $a$, $b$ and $c$ in Fig. 3(b). The higher intensity of the diffraction spots labelled $T_1$ suggest that the crystal orientation of the Ge is type B, consistent with X-ray pole figure analysis shown in Fig. 3(b). Fig. 4(e) shows a typical high-resolution TEM image of the grain boundary region in the Ge layer. The misorientation between the adjacent grains is <2°. These boundaries consist of a dislocation array and are known as small angle grain boundaries. To better illustrate this type of boundary, a schematic is shown in Fig. 4(f), where the dark lines represent the {1 1 1} and {2 0 0} planes visible in Fig. 4(e), the green lines represent {3 1 1} planes, the red dotted line represents the boundary and “…” represents a dislocation. The small angle grain boundaries in conjunction with X-ray pole figure and TEM analysis show that the Ge film deposited were quasi-single crystal.

It has been shown that the fluoride films grown on semiconductor (1 1 1) surface or semiconductor films grown on (1 1 1) fluoride surface have either type A, type B [14] or a mixed [15] epitaxial relation with the substrate. The epitaxial relation depends on the growth temperature, the ionicity of the substrate, and the lattice matching conditions between the film and the substrate [16–23]. In the case of epitaxial growth of semiconductor on single crystal CaF2 (1 1 1) surfaces, the semiconductor exhibited a type B orientation when the CaF2 surface was exposed to e-beam, ion-irradiation or high temperature prior to film deposition [19,20,24,25]. For the untreated CaF2 surfaces or when the substrate temperature was low, a mixed orientation (type A and type B) was observed. In our work, it was found that at lower growth temperatures such as 300 and 350 °C, the Ge films grown on CaF2 contained a mixed (type A as well as type B) epitaxial relation with respect to the substrate. Type A orientation seemed to gradually diminish at higher growth temperatures and at a growth temperature of 400 °C, the Ge grew primarily to be a type B film with respect to the CaF2 substrate. A higher temperature could aid to the dissociation of a larger fraction of F− from the interfacial layer of the CaF2(1 1 1) surface [26] similar to the effect of e-beam or ion-irradiation and if this happens, the Ge film deposited onto Ca2+ terminated CaF2(1 1 1) surface will have a type B epitaxial relation with respect to the CaF2 substrate.

4. Conclusion

In conclusion, high-quality biaxially textured Ge films were epitaxially grown onto a biaxial CaF2 buffered glass substrate held at elevated temperatures. From XRD and X-ray pole figure analysis, it was determined that the Ge film was amorphous at a growth temperature of 250 °C or lower and crystalline with biaxial texture orientation at temperature of 300 °C or higher. The Ge films contained a mixture of type A and type B epitaxy of Ge on CaF2 with type B epitaxy dominant at higher growth temperature. The film grown at a substrate temperature of 400 °C showed the best biaxial texture property with small angle grain boundaries (misorientation was less than or equal to 2°). In contrast, the Ge films grown on bare glass substrates without biaxial CaF2 layers were polycrystalline even at 400 °C substrate temperature. Our work showed that it is possible to grow quasi-single crystal Ge film with small angle grain boundaries on amorphous substrate with a biaxial CaF2 buffer layer.

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