Single-Crystalline-Like Germanium Thin Films on Glass Substrates

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***Abstract* — Single-crystalline-like germanium films have been demonstrated on inexpensive glass substrates (quartz). Ion Beam Assisted Deposition (IBAD) was employed to achieve biaxial crystallographic texture in MgO deposited on quartz substrates. Using intervening epitaxial oxide buffer layers, single-crystalline-like germanium films have been grown by magnetron sputtering. In-spite of significant lattice mismatch and structural mismatch, epitaxial growth was achieved in all layers. All thin films in this work were deposited by reel-to-reel processing. In-plane texture better than 5° has been measured in the germanium film. A Hall mobility value of 107 cm^2/Vs was attained in 400 nm thick germanium films on glass substrates.**

***Index Terms* — germanium, mobility, epitaxy, glass, quartz.**

I. Introduction

Thin film PV is typically referred to amorphous silicon, Cd-Te and CIGS technologies [1-3]. These technologies have been demonstrated on inexpensive substrates and by roll-to-roll manufacturing. However, the efficiencies of production thin film PV are less than one half that achieved with crystalline silicon. We have been pursuing the feasibility of thin film PV with III-V compounds for the reason that achievement of a combination of low cost and high efficiency would be game-changing in the PV industry.

Photovoltaic cells based on III-V compounds have exhibited efficiencies of about 40% [4], but have found only a use limited to utility-scale concentrator applications because of their cost, which is primarily driven by the high cost of single crystal substrates. III-V solar cells with efficiency greater than 20% was achieved with rigid, optical-grade polycrystalline germanium substrates 15 years ago [5], but no significant progress has been reported since. Additionally, a bulk polycrystalline Ge substrate is still an expensive proposition for solar cells.

Our approach is a process method to achieve single-crystalline-like epitaxial photovoltaic thin films on inexpensive polycrystalline substrates utilizing technology successfully demonstrated outside the PV industry for transmitting electric power. Our innovation lies in the creation of an architecture that yields single-crystalline-like thin films even on polycrystalline or amorphous substrates. The first enabler in the thin film multilayer architecture that was employed in this work is a biaxially-textured template made by Ion Beam-Assisted Deposition (IBAD) [6]. Such a texture is termed biaxial texture since grains are aligned in the plane along two crystallographic axes (in fact, grains are aligned in all three axes including the out-of-plane axis). IBAD template films have been successfully employed for epitaxial growth of oxide superconducting films on polycrystalline, flexible substrates with critical current densities as high as those achieved on single crystal substrates [7]. We had previously demonstrated that IBAD-based templates on flexible metal substrates can be used to fabricate single-crystalline-like germanium films with a good biaxial texture as well as excellent optical properties [8-12]. The refractive index and extinction coefficient of the Ge films on metal substrates have been found to be comparable with that of single crystal germanium [8]. GaAs has been epitaxially grown on single crystalline-like germanium on metal substrates [11]. The GaAs is found to exhibit strong photoluminescence signal and good optoelectronic quality [11]. In this paper, we report the development of single-crystalline-like germanium thin films on inexpensive *glass* substrates for high-efficiency, low-cost photovoltaics. Glass substrates are widely used with thin film silicon solar cells and hence, III-V solar cells on glass should be adaptable in the PV industry. Additionally, flexible glass substrates that are being developed can be employed for roll-to-roll manufacturing for lower-cost production. High mobility semiconductor films on glass substrates could also be used for other applications such as flexible displays.

II. Experimental

100 μm thick quartz substrates were used in this study. A schematic of the multilayer architecture that was fabricated in this study is shown in Figure 1. All films in the architecture were deposited by reel-to-reel processing with continuous substrate movement during deposition. The quartz substrates were mounted on a metal carrier and could be flexed over rollers used in the deposition systems during reel-to-reel processing. An amorphous layer of yttrium oxide was first deposited on the substrate by ion beam sputtering. This film provides a pristine surface for the growth of subsequent deposition of biaxially-textured MgO. Next, about 10 nm of MgO was deposited by ion beam sputtering at room temperature with simultaneous bombardment of the substrate with an Ar ion beam inclined at 45° to the substrate normal. Texture development during MgO growth is monitored with *in situ* Reflection High Energy Electron Diffraction (RHEED).

A homo-epitaxial MgO film, about 30 – 50 nm thick was deposited atop the IBAD MgO by reactive magnetron sputtering. We have found that for epitaxial growth of germanium on IBAD MgO templates, a fluorite material needs to be inserted as an intermediate layer [8]. In many cases, a perovskite $LaMnO_3$ is deposited epitaxially on the homo-epi MgO layer followed by cerium oxide deposition. All

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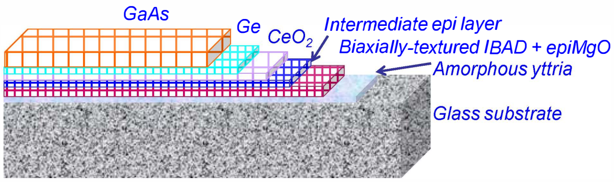

Fig. 1 III-V thin film architecture based on single-crystalline-like Ge film on quartz substrate.

materials are deposited by reel-to-reel magnetron sputtering at a temperature of about 800°C. As in the case of all oxide layers, germanium is also deposited by reel-to-reel magnetron sputtering on the epitaxial cerium oxide.

The out-of-plane texture of all samples was examined by theta-2theta measurements in X-ray Diffraction (XRD). Polefigures of selected samples were measured by GADDS XRD to determine the in-plane texture. Hall mobility values were measured at room temperature. Cross sectional microstructure of selected samples was examined by transmission electron microscopy (TEM). Samples for cross section analysis were prepared by focused ion beam (FIB) milling.

III. Results and Discussion

RHEED patterns were obtained during IBAD process to monitor development of crystallographic texture. Figure 2 shows the RHEED patterns of the IBAD MgO on quartz substrates as a function of the assist ion beam current. The ion beam current was increased from 84 mA to 92 mA, in intervals of 2 mA. All RHEED images were recorded when the patterns showed the maximum intensity for each assist ion beam current (I_a) value. Preferred orientation of the MgO film is observed starting at 84 mA. The biaxial alignment increases initially with increasing I_a, and then decreases when I_a is increased beyond an optimal value. Our result shows that the assist ion beam with I_a = 88 mA yield the best crystallographically-textured IBAD MgO on quartz substrate.

Next, the development of grain orientation in IBAD MgO film on quartz substrate at the optimized assist ion beam current value (I_a = 88 mA) with increasing time was studied and the results are shown in Figure 3. The RHEED images are found to change from a diffuse-scattering pattern to that showing clear crystalline texture. The diffraction spots intensify with further increase in time and then begin to degrade beyond an optimum time. This observation is similar to that observed in IBAD MgO growth on metal substrates.

A set of samples were fabricated with the optimized conditions of IBAD MgO growth on quartz substrate. Homo-epitaxial MgO, $LaMnO_3$ and CeO_2 layers were grown epitaxially on the IBAD MgO by reel-to-reel magnetron sputtering at temperatures of 750 to 825°C. A 400 nm thick Ge film was deposited at 825°C on the CeO_2 film by magnetron sputtering.

Theta-2theta X-ray Diffraction measurement was conducted on the germanium film grown on quartz substrate and the

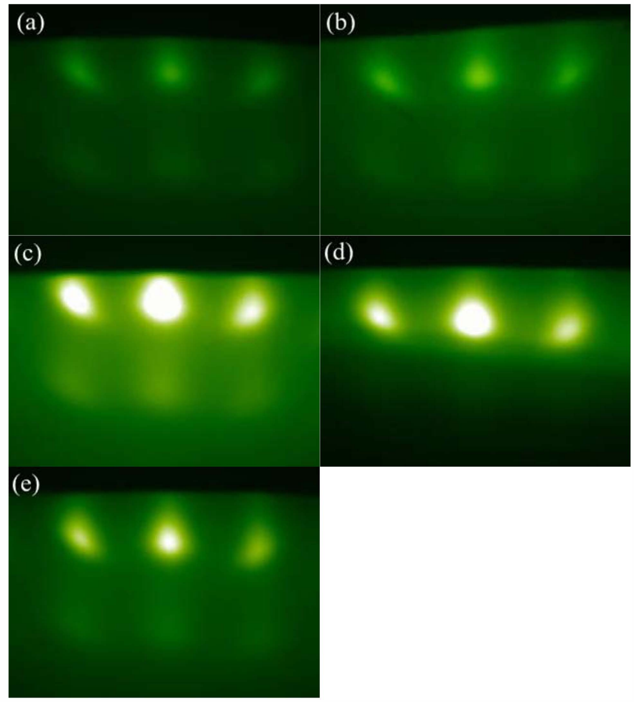

Fig. 2 RHEED images of IBAD MgO on quartz substrates with different assist ion beam current (a) 84 mA, (b) 86 mA, (c) 88 mA, (d) 90 mA, and (e) 92 mA.

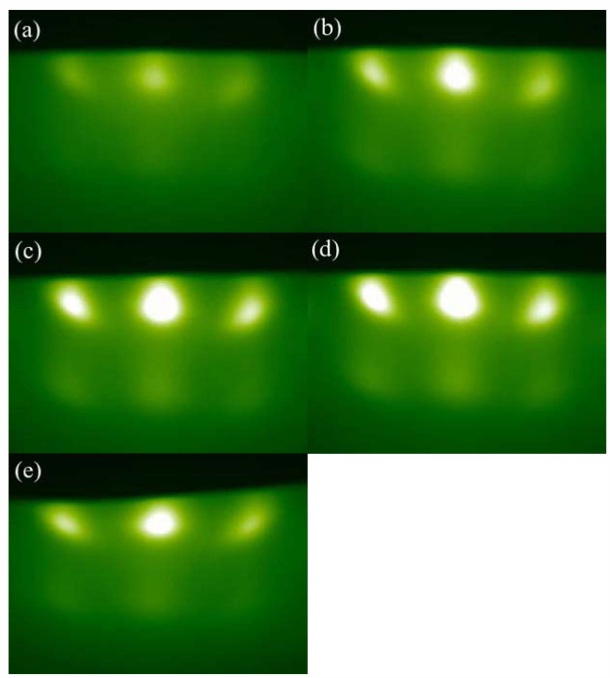

Fig. 3 Real-time RHEED observation of IBAD MgO film deposited on quartz substrate at I_a = 88 mA, in which images shown in (a) to (e) were obtained at 10, 30, 60, 85, 110 s from the onset of growth respectively.

result is shown in Figure 4. A shown in the figure, only the (h00) peaks of intermediate oxide buffers and germanium

(400) are prominent indicating the presence of a strong out-of-plane texture.

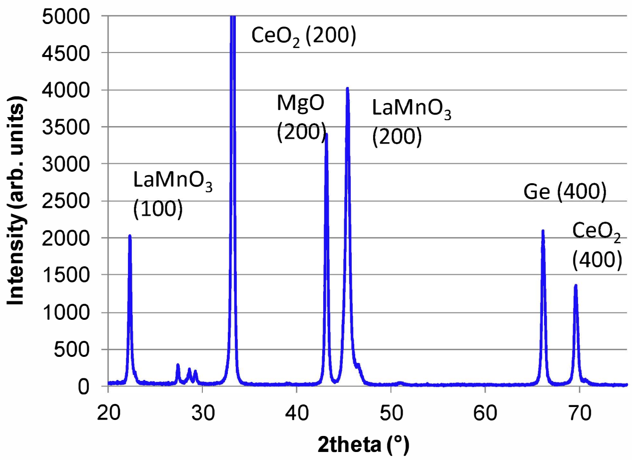

Fig. 4 Theta-2theta XRD pattern from a 400 nm Ge film deposited at 825°C on quartz substrate with intermediate epitaxial oxide buffers.

Figure 5 shows an (111) pole figure and Φ-scan of the Ge film deposited onto CeO_2 surface on IBAD MgO template on quartz substrate at 825℃. The pole figure and Φ-scan reveal a fourfold symmetry with the (111) poles at 55° with respect to the *c*-axis, indicating good in-plane alignment of the Ge films. The Φ-scans of Ge (111) peaks show four equally spaced peaks, separated by 90°, confirming the in-plane alignment of the Ge film. The full-width-at-half maximum (FWHM) of the Φ-scan peaks is found to be 4.5° for the Ge film deposited on quartz substrate. The polefigure in Figure 5 reveals additional peaks indicating some misoriented grains. In particular, there are low intensity Ge (111) peaks which lie at 16° with respect to the *c*-axis. These peaks are attributed to the crystal twinning which were observed in transmission electron microscopy described next. From the pole figure, we can also see there are some weak Ge (111) peaks oriented at 8°, 32° and 43° with respect to the *c*-axis.

Figure 6 exhibits a cross sectional microstructure of the single-crystalline-like Ge film developed on a quartz substrate. The crystal structure and lattice constants of the various epitaxial films in the architecture grown on IBAD template and the selected-area diffraction patterns (SADP) obtained from these films are shown in the figure. As seen in the SADPs, the germanium film is found to be epitaxial with a strong crystallographic preferred orientation. It is remarkable that epitaxial growth is maintained over four different crystal structures and a range of lattice parameters. Twin defects are seen in the germanium film originating at the CeO_2 interface and extending through the entire film thickness.

Hall mobility measurements conducted on germanium films on IBAD templates on quartz substrates showed values of 107 cm^2/Vs, which is comparable with those measured on germanium films of similar thickness on IBAD templates on metal substrates.

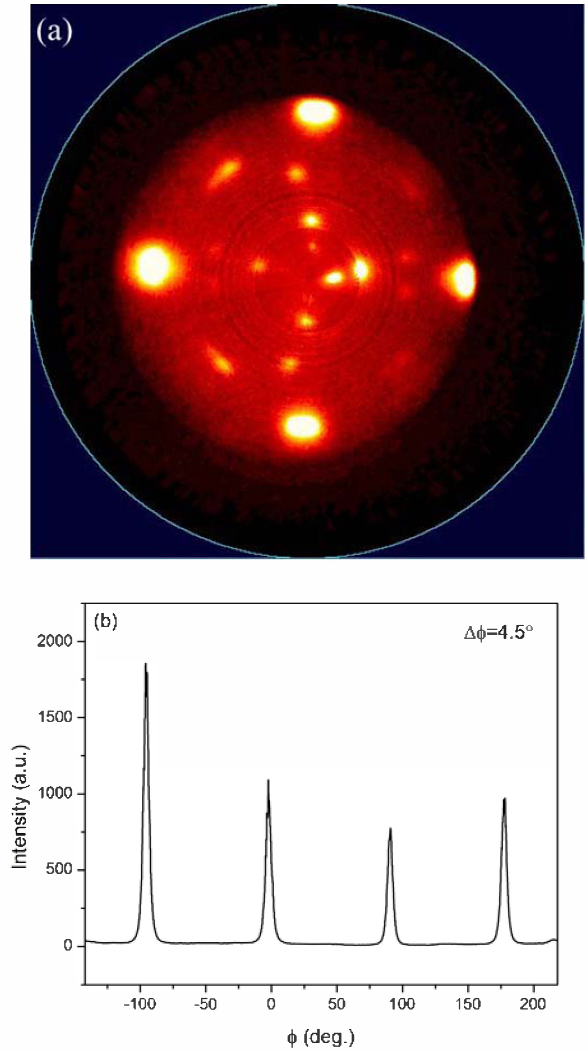

Fig. 5 (above) (111) pole figure and (below) Φ-scan of (111) peak from a 400 nm Ge film deposited at 825°C on quartz substrate.

IV. Conclusion

Single crystalline-like germanium films have been successfully grown on quartz substrate using biaxially-textured templates of MgO fabricated by Ion Beam Assisted Deposition. The optimum values of assist ion beam current and growth time were determined to achieve the sharpest crystallographic biaxial texture in IBAD MgO using in-situ RHEED pattern observations. Epitaxy is achieved in the germanium film via multiple oxide films with different crystal structures and a range of lattice parameters. (111) polefigure obtained from the Ge film on quartz substrate shows in-plane texture in the film better than 5° FWHM. The demonstration of single-crystalline-like germanium film on low-cost glass substrate enables the possibility of high-efficiency III-V PV at a low manufacturing cost.

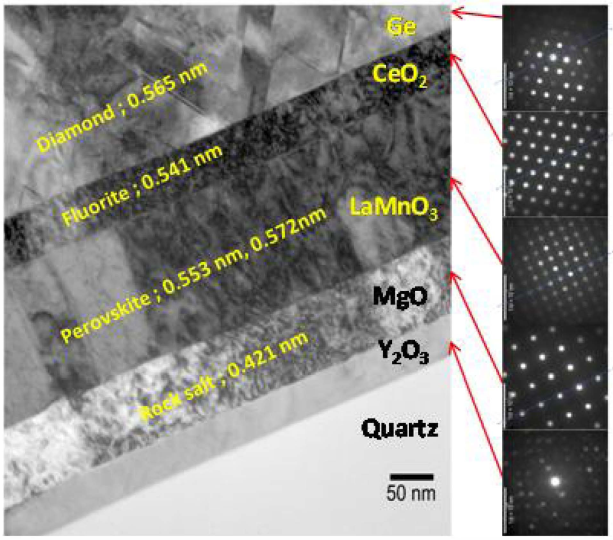

Fig. 6 Cross sectional TEM microstructure of single-crystalline-like Ge on IBAD MgO on quartz substrate with intervening epitaxial buffer films. Diffraction patterns from each layer are also shown.

V. References

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