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Highly textured silicon [111] crystalline thin-film on buffered soda-lime glass by e-beam evaporation

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ABSTRACT

A highly textured silicon [111] crystalline continuous thin-film film has been deposited on an MgO buffered soda lime glass substrate from an aluminum-silicon (Al-Si) eutectic melt using the conventional e-beam deposition. The silicon film growth was accomplished heteroepitaxially on the MgO buffered soda lime glass substrate. The resulting highly oriented crystalline film was then characterized by X-ray diffraction (XRD) and Raman spectroscopy for the detection of Si crystallization, as well as scanning electron microscopy (SEM). The low temperature Si crystallization method presented here requires no secondary annealing step and has the capability for high rate depositions without breaking vacuum. Furthermore, this method has the theoretical feasibility to induce single crystalline growth on the glass substrate, subsequently translating to a highly cost effective process with the potential to play a major role in the adoption of thin film silicon solar technology.

1. Introduction

It has been a long standing objective of the materials research community to grow single crystalline semiconductor thin-films, such as silicon, on inexpensive substrates such as glass or metal tapes. To date there are a number of research groups around the world who are actively working towards demonstrating high efficiency semiconductors or solar cells by trying to grow high quality semiconductor thin films such as silicon on inexpensive substrates. If a silicon thin film could be deposited onto soda-lime glass, for example, with quality comparable to that found in the silicon single crystals used in the microelectronics industry, the cost of photovoltaic technology would drop significantly [1]. Preliminary data we have gathered indicates that significant progress towards meeting this goal has been achieved. We fabricated a highly textured MgO buffer layer on glass substrate followed by in situ growth of a Si thin film on the buffer layer from an Al–Si eutectic melt prepared at 585 °C by the common e-beam evaporation technique. MgO is highly transparent (index of diffraction $n \sim 1.73$) in UV–vis–NIR wavelength regions and can be textured with uni- or biaxially crystalline orientations [2]. In organic solar cell technology, MgO has been found to be useful as a hole-transporting layer for improving charge collection efficiency [3]. In recent years MgO has also been introduced by Teplin et al. as a buffer layer on soda-lime glass for growth of polycrystalline Si films toward development of low cost solar cells and other potential electronics [4]. Textured crystalline MgO buffer layers may allow for growth of large grained Si thin films with a preferred crystalline orientation on glass. Like ZnO [5], MgO can also provide enhanced light trapping for solar cells by the textured surface morphology. In addition, it can modify the properties of soda-lime glass, reducing, for instance, the effect of the glass strain point temperature of ~450 °C) [6], which has been found to adversely affect the crystallization in Si thin films due to the temperature increase of the glass substrate [7]. Additionally, MgO buffer films serve as a chemically compatible and preventative metal diffusion barrier. Finally, the crystal structure of MgO also provides a chemical and crystalline order that positively aids heteroepitaxial Si growth.

2. Materials and methods

The MgO buffer film was deposited using an e-beam evaporation system at Blue Wave Semiconductors. For the 7 μm MgO deposition, a 3.2 mm thick slice of soda lime glass, manufactured by Taiwan Glass, served as the substrate. The selected buffer film deposition temperature was 550 °C, a temperature below the

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softening point of ordinary soda-lime glass. For MgO growth, a Blue Wave Semiconductors™ electron beam evaporation system with substrate temperature controls was utilized. The evaporation source was highly dense MgO crystals. The source to substrate distance was between 6 and 9 in. and the deposition rate was monitored by a quartz crystal thickness monitor. Base pressure in the vacuum chamber was held at 10^{-7} Torr [8]. After deposition samples were cooled at 30 °C/min rate. In two previous papers, we reported that samples made by the same process were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) [9,10]. Next, following the approach disclosed by P. Chaudhari, [11], silicon was deposited on the MgO substrate by the following steps: using a thermal evaporator, a 40 nm Al layer was deposited onto the MgO buffer under moderate vacuum conditions of 10^{-5} Torr. The sample was then manually removed from the thermal evaporator, placed into the electron beam evaporator and taken to a vacuum level of 10^{-7} Torr. A 200 nm Si thin film was subsequently deposited onto the Al layer while the substrate was held at the constant temperature of 585 °C (above the Al–Si eutectic temperature of 577 °C, but below the softening temperature of soda-lime glass which is ~600 °C). The deposition rate of Si was held constant at 6 nm/min. Upon completion, the system was then cooled to room temperature, allowing the film to phase separate into aluminum and a crystalline film of silicon on the MgO buffer. The sample was removed from the chamber and characterized using X-ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM).

3. Results

The analysis concluded that there was continuous, highly textured silicon formation with crystallites of aluminum throughout. An XRD scan which illustrates the polycrystalline nature of the Al–Si eutectic film on MgO buffered soda-lime glass is illustrated in Fig. 1.

Consistent with data previously reported on in this journal regarding the MgO [12], two very strong reflection peaks are seen at 36.95° and 78.6°. The first of these can be identified as MgO [111] based on the characteristic peak for MgO observed at 36.93° [13]. The second can be identified as MgO [222] and is the associated parallel peak for MgO, again based on the known characteristic peaks for MgO [14]. Other characteristic MgO peaks manifest at 42.90° [200] and 74.67° [311]. There are several small peaks found at 37.95°, 44.2°, 63.85°, 70.42° and 77.9°. These peaks can be identified as Al [111], Al [200], Al [220], Al_2O_3 [125] and Al [311] respectively, based on the known characteristic peaks for Al and Al_2O_3 observed at these positions. Finally, the Si [111] peak can be seen at 28.35° as expected. The card files used here for MgO, Al, Al_2O_3, and Si are 04-0829, 03-0932, 82-1468, and 77-2111 from the JCPDS – International Centre for Diffraction Data respectively [15].

RAMAN analysis was conducted to corroborate the crystallinity of the Si/Al films measured by the XRD data. Fig. 2 illustrates the Raman Si peaks along with Gaussian fitting functions.

Fig. 2(a and b) representatively shows Raman spectra with Richter–Campbell–Fauchet (RCF) fitting for the sample before and after Al etching [16,17]. A relatively sharp and symmetric Raman band between 519.8 cm^{-1} and 520.6 cm^{-1} is seen in the samples, indicating the formation of crystalline Si phase in the film. Fig. 2c shows a single crystalline Raman spectrum overlaying the MgO/Si film Raman spectra.

While the growth of high quality silicon shown here is of major importance, the silicon must also be continuous to be functionally utilized in commercial applications. An SEM image of the Si crystalline layer on top of the MgO elucidates the continuity of the film is shown in Fig. 3a.

4. Discussion

XRD spectra revealed that a silicon crystalline film has successfully been grown on the MgO substrate and given that there is only one Si peak, [111], the film can be characterized as highly textured. Given the intensity of the MgO peaks and the thickness of the film (7 μm), it is likely that the Si peak intensity in the XRD appears smaller than it otherwise would. The MgO peaks reveal a highly textured MgO [111] film, which has successfully been grown again, confirming data previously reported in this journal, and moreover the associated parallel [222] peak indicates that a high level of crystallinity has been obtained. The MgO data and peaks reported here are virtually no different than those peaks seen in single crystal MgO [111] XRDs [18].

A relatively sharp and symmetric RAMAN band at 519.8 cm^{-1} is seen (see Fig. 2a), indicating the formation of crystalline Si phase

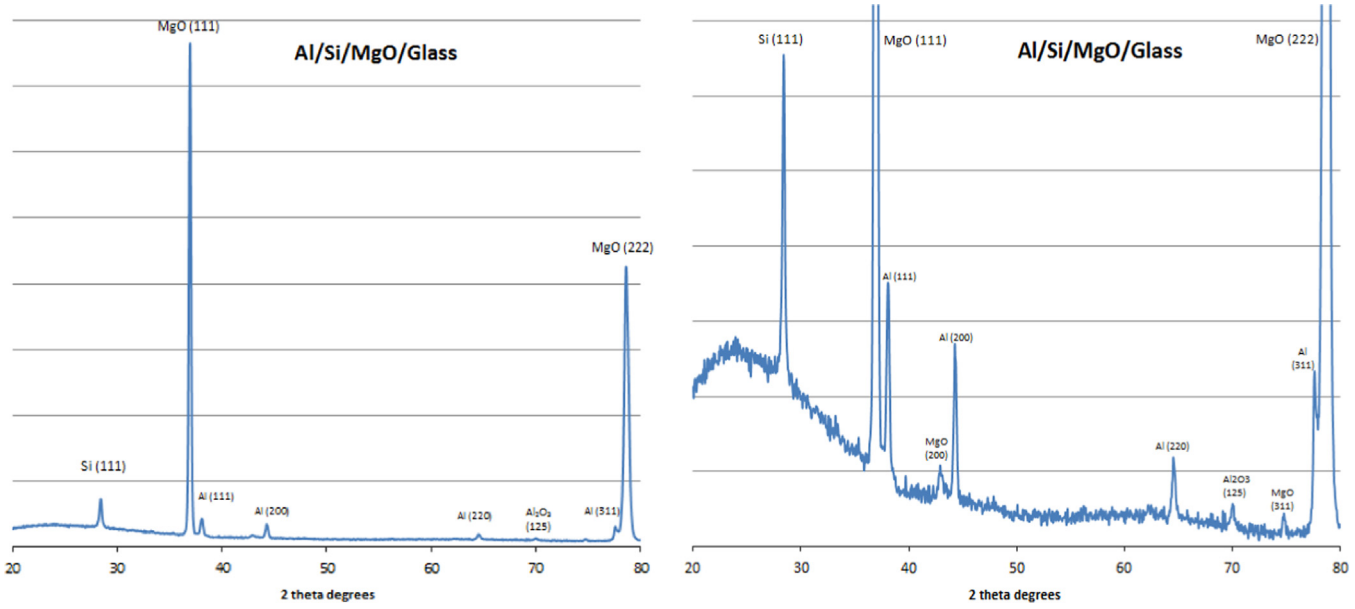

Fig. 1. XRD of Al–Si on MgO on soda-lime glass with zoomed in image on right.

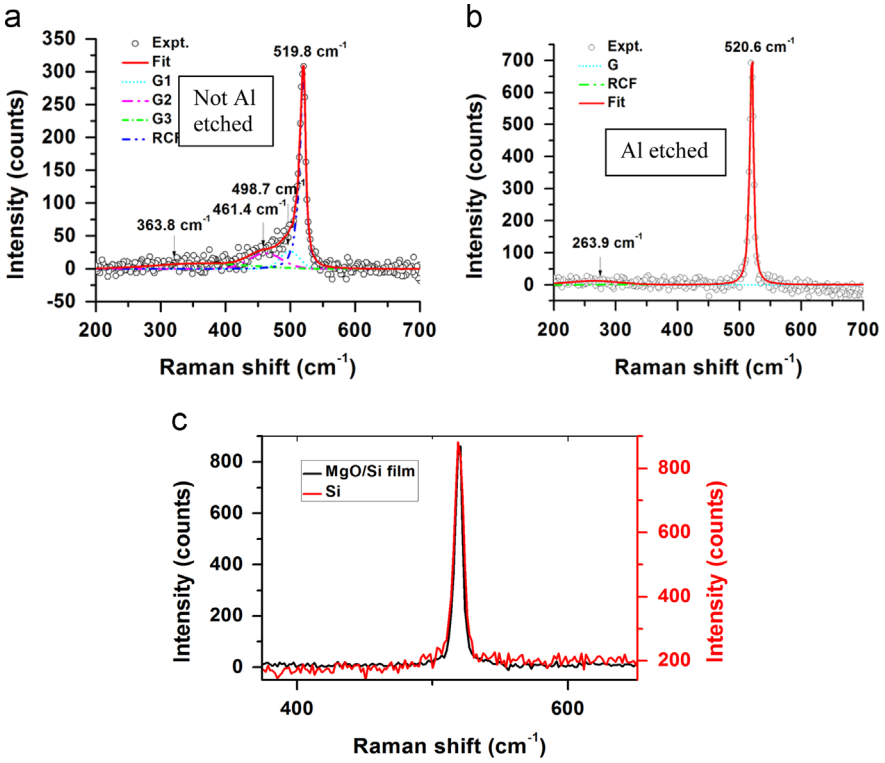

Fig. 2. Raman analysis of Si nanoparticles on MgO/soda-lime glass using the Richter–Campbell–Fauchet (RCF) phonon confinement model and fitting.

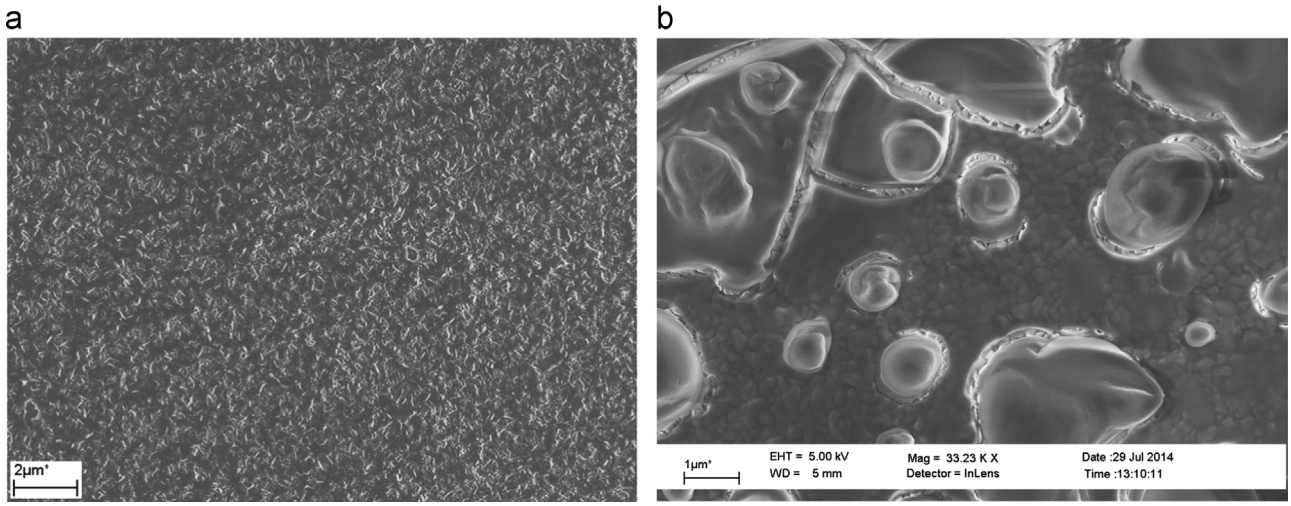

Fig. 3. (a) SEM image of the Si crystalline layer on top of the MgO buffered soda-lime glass substrate, after Al etching, elucidating the continuity of the film. (b) SEM image of the same sample as in Fig. 3a prior to etching of the Al, clearly showing the Si layer underneath the Al.

in the film. There is also an amount of amorphous Si phase visible from the RAMAN bands at the wavenumber below 500 cm^{-1} in the figure. The amorphous phase possibly exists in the mixture with Al on the sample surface and may be in a pure state as well from not undergoing eutectic mixing with Al as a melt for crystallization due to the thickness ratio of Al to Si and the textured or rough morphology of MgO. Such a buffer layer effect is expected as it has been observed that there is a significant difference of Si nucleation on ZnO:Al coated and non-coated glass substrates [19]. Considering these effects, we performed a brief etch of the sample with a sodium hydroxide/water solution. Upon completion, the spectra in Fig. 2b displays a sharp and symmetric Raman band of crystalline phase Si, centering at 520.6 cm^{-1}, without an observable amorphous-phase Raman scattering. The estimated grain sizes by RCF model are 18.7 nm before etching and 31.8 nm after etching on average from different areas sampled [20]. The comparison of the Raman spectrum with that of a single crystalline Si wafer (Fig. 2c) clearly evidences the establishment of polycrystalline or perhaps single crystalline Si film quality with the MgO buffered sample based on the excellent spectral match between the sample and Si wafer. The epitaxy-like growth of Si is confirmed by the observation of only Si (111) preferred crystalline orientation in the XRD pattern shown in Fig. 1. The coincidence of the same Si (111) orientation of the grown film with the (111) textured MgO buffer layer strongly suggests the epitaxy-like growth of Si is attributed to the lattice platform provided by the highly crystalline MgO buffer layer. The results prove both the achievement of crystalline MgO growth in the present work and the usefulness of such a layer for controlling the subsequent crystalline growth of Si thin layer. Following the recipe of Chaudhari [21], a thicker Si film can now be induced to

grow on the crystalline Al etched Si film grown here. Such a film could potentially be single crystalline, and in the very least it is likely that it would be highly textured. A solar cell device based on this Al–Si on MgO on soda-lime glass material would be a major breakthrough due to cost of production, given that: (1) the Si film in such a device would only need to be ~20 μm in order to approach the efficiency of monocrystalline solar cells (the current wafer thickness of monocrystalline solar cells is ~140 μm) [22]; (2) both MgO and soda-lime glass are inexpensive materials; (3) the MgO buffer protects the Si film from impurities found especially in cheap glass; (4) the deposition process only requires the conventional e-beam method; (5) there is no high vacuum required (beyond 10-7E Torr) which is an additional cost savings; (6) there is no annealing step which saves time and energy; (7) the metal used is cheap Al and is recyclable; and (8) Al serves as P type dopant in the Si film necessary for solar cell device fabrication.

5. Conclusion

XRD, RAMAN, and SEM noticeably show that a highly textured Si thin-film has been successfully grown on an extremely textured MgO [111] film on soda-lime glass substrate. The results demonstrate that a metal oxide buffer can be incorporated into a simple method to fabricate high quality Si crystalline films on cheap soda-lime glass substrates, as an additional control parameter for manipulating the film growth. Further work to understand the interplay between MgO crystalline orientations, uni- or biaxially texturing, thickness ratio of Al to Si, and the Si film quality is important to the final device performance. In the future we plan to do more testing and characterizations which will include refining the process described above by lowering the amount of Al in order to more closely resemble the modified vapor–solid–liquid (VLS) process disclosed by P. Chaudhari. [23].

6. Funding/sponsor

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