

Crystalline Al₂O₃ on buffered soda-lime glass by e-beamAshok Chaudhari^{a,*}, R.D. Vispute^b, Thomas M. Murray^c, Harry Efstathiadis^c^a Solar-Tectic LLC, 416 Long Hill RD E, Briarcliff Manor, New York, USA^b Blue Wave Semiconductors, Inc., BW Technology Center, 1450 South Rolling Road, Suite 4064, Baltimore, MD 21227, USA^c SUNY – College of Nanoscale Science and Engineering, 257 Fuller Road, Albany, NY 12203, USA

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ABSTRACT

We report for the first time the successful deposition of a continuous crystalline Al₂O₃ film on ordinary soda-lime glass via an extremely highly textured MgO buffer layer, using the ordinary electron-beam evaporation method. As a result, a highly crystalline thin-film of silicon may now be deposited on inexpensive Al₂O₃ buffered soda-lime glass for cost-effective photovoltaic and other electronic applications. In addition, our results have made possible a new kind of inexpensive and light-weight “sapphire glass” that can be used for display covers for smartphones etc.

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1. Introduction

Growth of high quality crystalline semiconductor films on inexpensive substrates has been of considerable interest to a number of research groups around the world due to the cost saving potential of devices made from such films. For example, high quality crystalline silicon thin-film on glass could replace the relatively expensive 140 μm silicon monocrystalline wafer currently used in the solar industry while maintaining efficiency of light conversion [1]. It has long been known that single crystalline silicon can be deposited heteroepitaxially on single crystalline sapphire (Al₂O₃). This is a well-known commercial process. However, sapphire is not an inexpensive substrate¹ [2]. It has been suggested therefore that sapphire be grown as a thin-film or template on glass, and then Si deposited on it [3,4]. Here, for the first time, we report growth of a continuous crystalline α-Al₂O₃

film on ordinary soda-lime glass via a crystalline MgO buffer layer, by the common e-beam method.

Findikoglu et al. were the first to demonstrate that crystalline Al₂O₃ could be deposited on MgO for purposes of Si film growth and device fabrication [5]. Their substrates were both amorphous glass and polycrystalline metal-alloy tapes. Moreover, the buffer layers they used were also MgO and Al₂O₃ in that order [6]. However, there are major differences from their results and what we are reporting here. They are: 1) the glass they used was borosilicate with a softening point of 985 °C [6] whereas we have used ordinary soda-lime glass; 2) they used γ-Al₂O₃ and the grain sizes of their films were not reported (for either glass or tapes)²; 3) their process required use of Ion Beam Assisted Deposition (IBAD) and a nucleation layer, adding to the cost and complexity of the process. [7] Thus, growth of highly oriented or single crystal silicon films on glass via a sapphire (crystalline α-Al₂O₃) layer, or any other template for that matter, that is cost-effective, has not been achieved despite many efforts.

In order to succeed with this approach, the aim is to: 1) deposit a single crystal (or large grained, highly textured) template of Al₂O₃ (sapphire) and 2) grow single crystal or oriented thin films on it at temperatures below the melting point of the glass substrate,

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¹ As a result of Apple Inc.'s recent R&D, the cost of sapphire may drop significantly in the near future as they have announced a massive sapphire initiative and have disclosed a technology for making sapphire laminates or sheets of single crystal sapphire on inexpensive substrates which could be used as substrates for single crystal silicon solar cells. Their technology has not as of the date of this paper been made available to the public either for licensing or for purchase as a product.

² Teplin et al. reported that Findikoglu demonstrated high mobility in heteroepitaxial silicon layers on small (< 0.6 μm) grains of biaxially textured γ-Al₂O₃ buffers deposited on by e-beam on MgO-coated Hastelloy foils. See “Heteroepitaxial film crystal silicon on Al₂O₃: a new route to inexpensive crystal silicon photovoltaics” Energy Environ. Sci., 2011, 4, 3346.

or $\sim 600^\circ\text{C}$. Recently it was shown that single crystalline silicon can be deposited heteroepitaxially on sapphire below the melting point of glass (600°C) [8]. However, an Al_2O_3 template on soda-lime glass of sufficient crystalline quality has not yet been achieved. Here for the first time we report an important preliminary step in the direction of meeting this goal, having successfully grown $\alpha\text{-Al}_2\text{O}_3$ with adequate crystallinity on ordinary soda-lime glass using the common e-beam method. With this result we expect to be able to deposit highly textured [111] oriented silicon films on it (and perhaps even a single crystalline film) below the melting point of the underlying glass substrate, using our proprietary eutectic deposition method reported on previously [9], along with the process invented by P. Chaudhari [10]. The reasoning for this is that crystalline alumina (Al_2O_3) with preferred orientation can act as a seed for initial nucleation of Si or an Si-metal eutectic in order to lock the required silicon orientation. In the post-nucleation scenario, silicon or an Si-metal eutectic then has the choice to grow laterally (into large grain oriented films) [14] or vertically (nanowires or tubes or whiskers). On the whole, this is a kind of modified Vapor–Liquid–Solid (VLS) technique which is applied to thin films for the first time [15].

2. Materials and methods

A film of extremely highly textured [111] MgO was first deposited on soda-lime glass. The MgO film was deposited using

an e-beam evaporation system. For the $7\ \mu\text{m}$ MgO deposition a $3.2\ \text{mm}$ thick regular soda lime glass (basically window glass), manufactured by Taiwan Glass in Taiwan was used. The MgO was deposited at the substrate temperature of 550°C (below the softening temperature of soda-lime glass) by e-beam evaporation using a “Blue Wave SemiconductorsTM” made vacuum system. The evaporation system was equipped with the capability of holding the substrate – in this case soda-lime glass – at a specific growth temperature necessary to control growth kinetics. The evaporation source was highly dense MgO crystals. The source to substrate distance was between 6 and 9 in. The deposition rate was monitored by quartz crystal thickness monitor. Base pressure in the vacuum chamber was achieved to be better than $10\text{E} - 7$ Torr. After deposition the sample was cooled at $30^\circ\text{C}/\text{min}$ rate. After preparation of the MgO on glass sample, a $500\ \text{nm}$ thick layer of Al_2O_3 was deposited on top using the same equipment and process.

3. Theory/calculation

N/A.

4. Results

X-Ray diffraction (XRD) (see Fig. 1) showed the expected peaks for crystalline MgO based on our previous work [11] a strong [111]

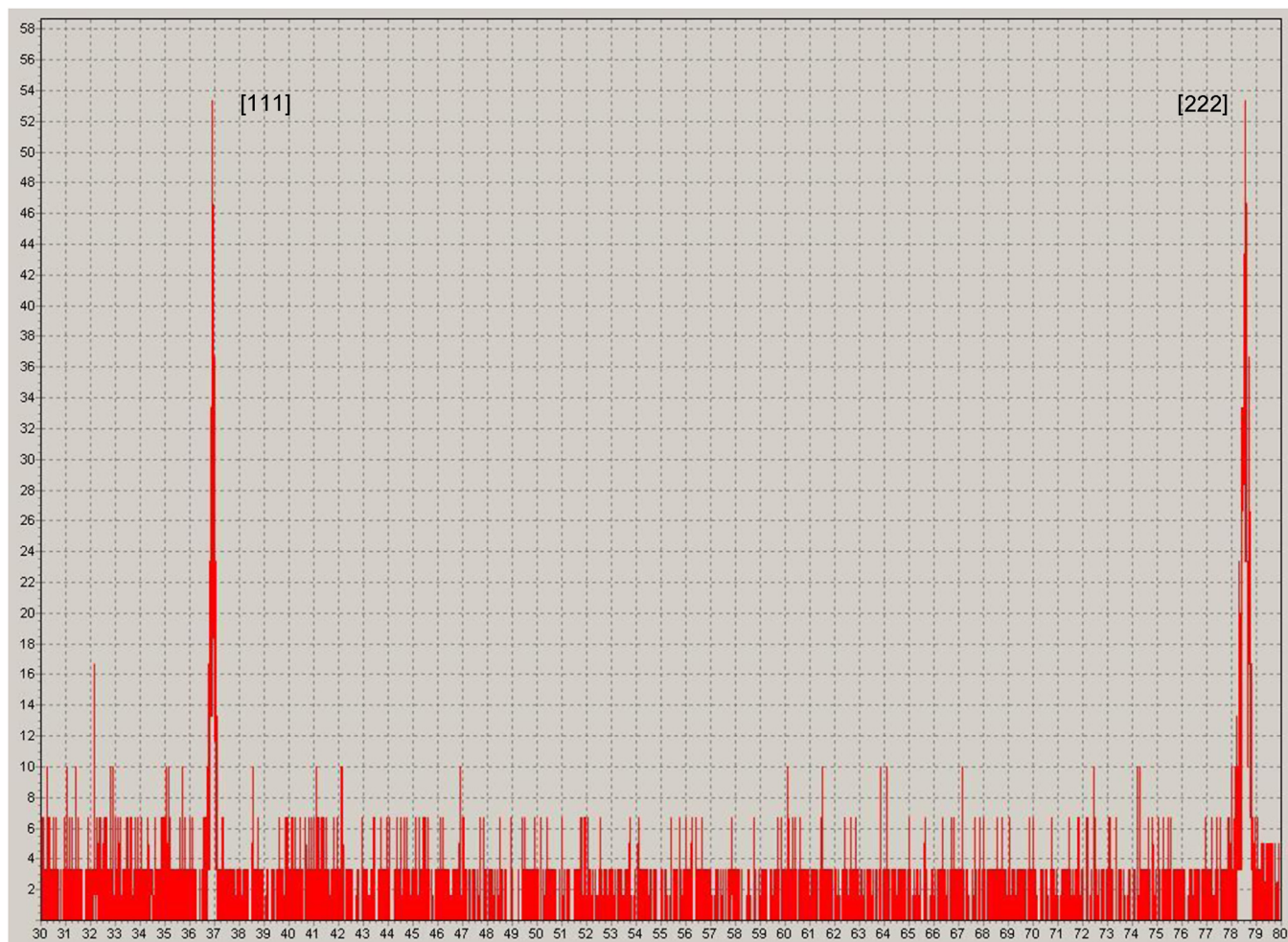


Fig. 1. XRD of $7\ \mu\text{m}$ MgO on soda-lime glass (Miller indices added).

peak found at ~ 37 deg. and the associated parallel peak [222] found at ~ 78.6 deg. [12]. Importantly, these results are very similar to MgO **single crystal** [111]. XRD of the $\text{Al}_2\text{O}_3/\text{MgO}$ on glass was also performed (Fig. 2) and again showed the same peaks for MgO, but no substantial peaks for Al_2O_3 were visible.

Next, Transmission Electron Microscopy (TEM) was performed on the sample (see Fig. 3).

TEM clearly showed the MgO and Al_2O_3 material and layers and confirmed that a ~ 500 nm Al_2O_3 layer had been grown. Also, the Al_2O_3 layer showed fine, small crystals.

A closer image was needed for better visibility of the crystals (see Fig. 3).

The image clearly showed tweed-like crystalline patterns in both the MgO and Al_2O_3 materials.

In order to further investigate the crystallinity of the Al_2O_3 layer, the main material of interest here, diffraction was taken further away from the MgO/ Al_2O_3 interface see also Fig. 4.

The diffraction from the Al_2O_3 layer showed that it is polycrystalline with fine crystallites.

5. Discussion

XRD of the $\text{Al}_2\text{O}_3/\text{MgO}$ sample showed that an extremely highly textured MgO [111] continuous film had been grown on soda-lime glass, consistent with our recently reported results [13]. Also, the associated [222] reflection peak for MgO at 78.6 deg. was visible which is an indicator of crystalline quality. While XRD showed no substantial peaks as evidence of Al_2O_3 crystallization, TEM images and diffraction data unequivocally demonstrated that a continuous Al_2O_3 crystalline film had been achieved. The crystals appear to be very fine, and we estimate the size to be between 10 and 20 nm which is substantial given our purposes, though clearly not large. This grain size estimate needs to be confirmed by further

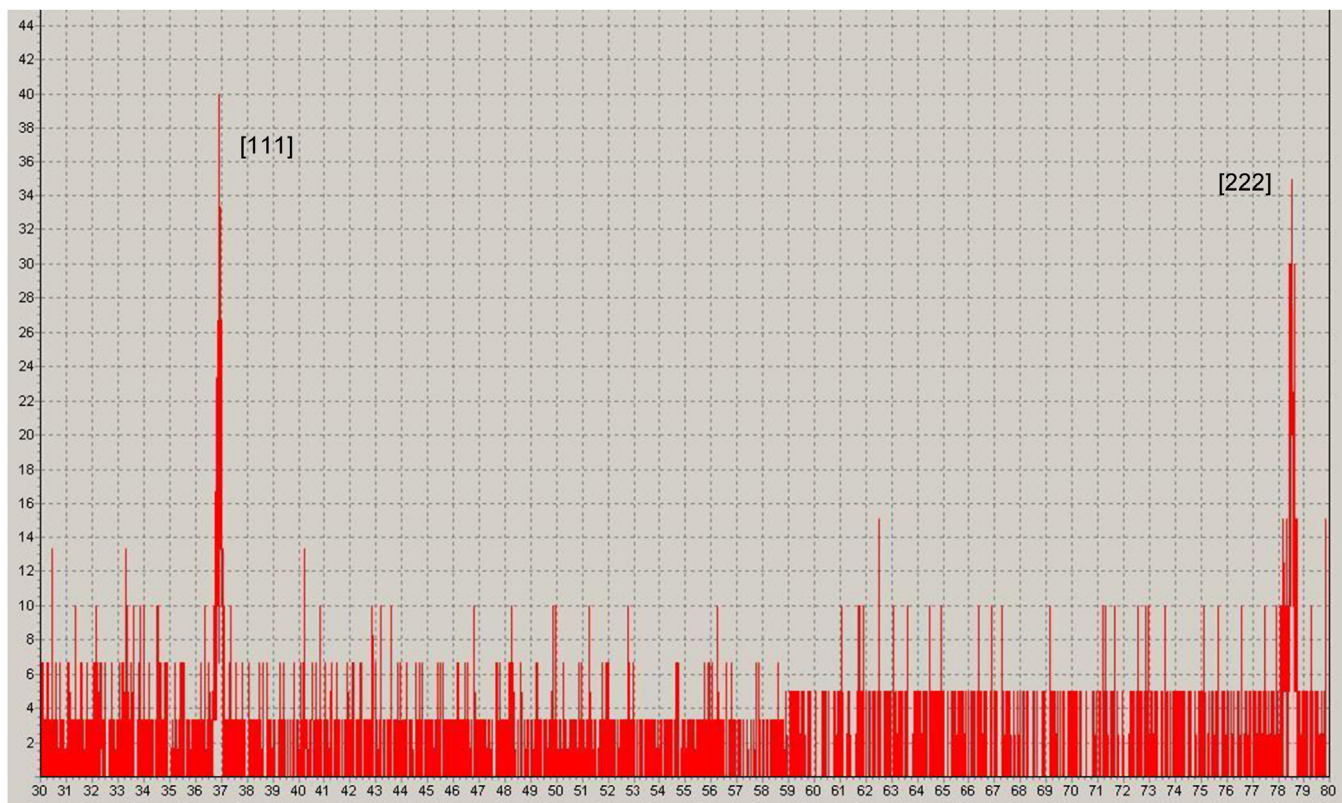


Fig. 2. XRD of 500 nm $\text{Al}_2\text{O}_3/7 \mu\text{m}$ MgO on soda-lime glass.

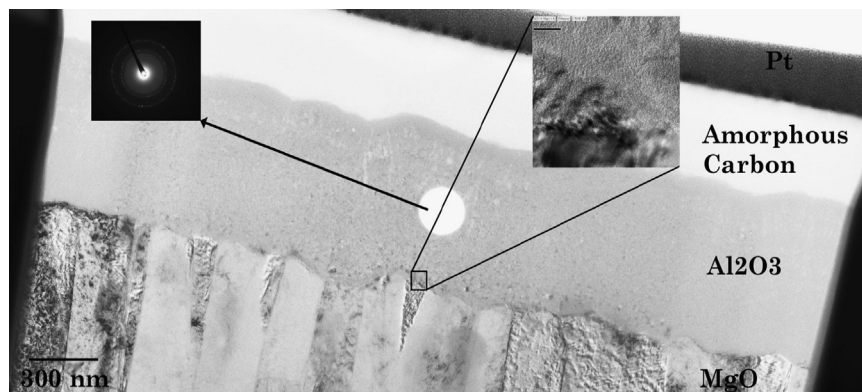


Fig. 3. Image showing 1) TEM of 500 nm $\text{Al}_2\text{O}_3/7 \mu\text{m}$ MgO on soda-lime glass; 2) a continuous film of MgO and Al_2O_3 ; 3) a close-up image of 500 nm Al_2O_3 on 7 μm MgO on soda-lime glass at the MgO/ Al_2O_3 interface; 4) diffraction of area selected further away from $\text{Al}_2\text{O}_3/\text{MgO}$ interface.

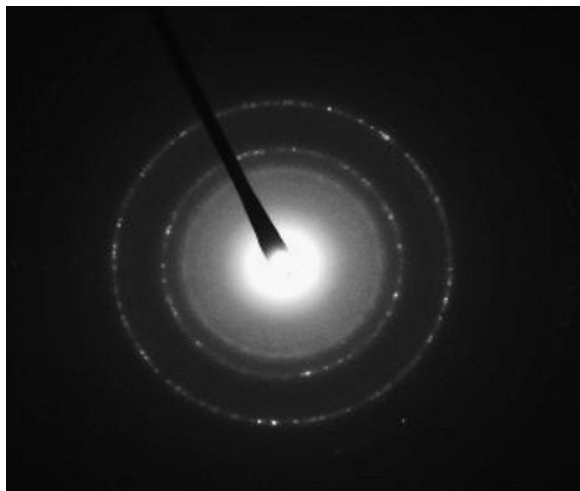


Fig. 4. Diffraction of area selected away from $\text{Al}_2\text{O}_3/\text{MgO}$ interface, enlarged.

characterization work, which is also needed for more information about the grain orientations. (For deposition of a textured silicon film [006] or [113] Al_2O_3 (or *c*-axis) would be a preferable orientation.) The fact that no Al_2O_3 peaks were visible in the XRD is likely due to the small grain size. Al_2O_3 has a small x-ray scattering because of low atomic mass which also contributes to a poor XRD for small grain size films. An additional issue is whether the Al_2O_3 crystals have in-plane and out-of-plane texture; that is, whether or not they are uniaxial or biaxial. We plan to investigate this in the near future.

As already stated, small grain sized α -alumina (Al_2O_3) with preferred orientation can act as a seed for initial nucleation of Si or a Si-metal eutectic in order to lock the required silicon orientation. In the post-nucleation scenario, silicon or a Si-metal eutectic then has the choice to grow laterally into large grain oriented films or grow vertically into nanowires or tubes or whiskers which are single crystal.

6. Conclusion

Having achieved continuous α - Al_2O_3 crystalline film growth on soda-lime glass by the conventional e-beam deposition tool for the first time, we have provided a preliminary step to growing highly textured polycrystalline (and possibly single-crystal) Si for further

deposition of a thicker ($\sim 20\ \mu\text{m}$) high quality silicon (and other semiconductor films) film from a eutectic melt, following the recipe disclosed by P. Chaudhari. Thus, a high quality crystalline silicon thin film can now potentially be deposited on ordinary soda-lime glass for breakthrough applications in the solar and display industries. In the future we plan to perform such depositions for PV and other applications, and we plan to continue to investigate and improve the $\text{Al}_2\text{O}_3/\text{MgO}$ on glass structure for a new kind of inexpensive, light-weight “sapphire glass,” as both MgO and Al_2O_3 are transparent.

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