Next Generation High-Efficiency Low-cost Thin Film Photovoltaics

Investigators

Bruce Clemens, Professor, Materials Science and Engineering, Stanford University
Alberto Salleo, Assistant Professor, Materials Science and Engineering, Stanford University

Robert Hammond, Senior Research Associate, Stanford University

James Groves, Technical Staff Member, Los Alamos National Laboratory

Joel Li, Garrett Hayes, Graduate Researchers, Stanford University

Howard M. Branz, Principle Scientist, National Renewable Energy Laboratory

Charles W. Teplin, Falah Hasoon, Senior Scientists, National Renewable Energy Laboratory

Vincenzo LaSalvia, Research Technician II, National Renewable Energy Laboratory

Abstract

Our goal is to develop novel growth approaches for producing low cost solar cells that have efficiency comparable to those made from high-cost, single-crystalline materials. Our efforts to date focus on using ion beam assisted deposition (IBAD) to control the grain boundary alignment in polycrystalline silicon thin films. The boundaries between highly aligned grains have smaller defect densities, which lead to higher carrier mobilities and lifetimes. Our approach can be extended to other thin film PV systems. In this initial period, we have produced highly aligned Si films by using a biaxially textured template layer of CaF_2. We have chosen CaF_2 as a candidate material due to its close lattice match with silicon and its suitability as an ion beam assisted deposition (IBAD) material. We show that the IBAD produces biaxially textured CaF_2 at a thickness of ~10 nm and, with the addition of an epitaxial CaF_2 layer, has an in-plane texture of ~15°. Deposition of a subsequent layer of Si aligns on the template layer with an in-plane texture of 10.8°. The additional improvement of in-plane texture is similar to the behavior observed in more fully characterized IBAD materials systems. A germanium buffer layer is used to assist in the epitaxial deposition of Si on CaF_2 template layers and single crystal substrates. These experiments confirm that an IBAD template can be used to biaxially orient polycrystalline Si.

Anticipating improved control of the texture with the IBAD process, we also investigated the ultimate limit of seeded orientation of silicon by growing silicon on CaF_2 that is epitaxially grown on single crystal yttria-stabilized zirconia (YSZ) with an extremely high degree of orientation. This approach yielded Si films with in-plane orientation of about 0.7°, showing that the heteroepitaxial growth of Si on highly oriented seeds will produce a very high degree of texture.

Recent work has led to improvement in the in-plane texture of the Ge layer on IBAD CaF_2/glass substrates to 5.04^{o} FWHM. The first solar cell device that we have fabricated exhibited an open-circuit voltage, V_{oc} of 444 mV and efficiency of 1.9%. This V_{oc} is

higher than what would be achieved with similarly-fabricated un-oriented polycrystalline silicon.

Introduction

The solar cell market is currently dominated by crystalline silicon modules due to their high efficiency and reliability. The cost of electricity produced by crystalline silicon panels however is still significantly higher than the cost of today's grid power ($0.27/kW.hr vs. $0.06/kW.hr). As a result, in order to increase the deployment of solar power, there is a need for new technologies to both decrease the cost and increase the efficiency of photovoltaics (PVs). Thin-film solar cells offer the opportunity to dramatically lower the price of solar energy by using small amounts of materials and low-cost manufacturing technologies. Ultimately, the efficiency of inorganic thin film solar cells is fundamentally limited by the fact that the active layers are polycrystalline and therefore by definition contain defects. In particular, recombination of photogenerated carriers at grain-boundaries is extremely detrimental to the efficiency of thin film solar cells.[1] Thus, a technology that drastically reduces the density of minority carrier recombination sites at the grain-boundaries of inorganic thin films would clearly be a step-out innovation as it would allow thin film PVs to approach the performance of single crystal devices at a fraction of the cost. Such devices constitute the next generation thin film PVs.

Here we propose to develop ion-beam based processing strategies that reduce grain boundary misalignment in polycrystalline inorganic thin films. Reducing the relative misalignment of neighboring grains will lead to lower recombination rates at grain-boundaries. We will thus create polycrystalline solar cells with power conversion efficiencies approaching those of their single crystal counterparts. In this exploratory proposal we concentrate on Si PVs because they constitute a well-known and controlled system and because of their relevance in the marketplace. The process we will develop however is quite general and could be applied to many other polycrystalline thin films systems, such as $CuInGaSe_2$ (CIGS) or Cu_2ZnSnS_4 (CZTS).

Solar cell efficiency is a strong function of minority carrier lifetime, since photo-generated carriers that recombine before reaching the p-n junction do not contribute to photocurrent. Grain boundaries in polycrystalline silicon films provide electron traps that act as recombination centers that reduce minority carrier lifetimes [1]. This recombination is a function of the grain boundary structure. In particular, the high dislocation density of high angle grain boundaries result in higher recombination rate than low angle grain boundaries. Dimitriadis et al. showed that the effective carrier lifetime increases as the dislocation density decreases [2], and in an elegant experiment using electron beam induced current contrast ratios in polycrystalline silicon films, Seifert et al. showed that recombination is a strong function of grain boundary defect density [3].

Grain boundaries can be described as having both out-of-plane and in-plane misorientation known as tilt and twist, respectively. Both types of misorientation result in defect densities that lead to recombination. The degree of tilt and twist in a thin film grain boundary population reflects the crystallographic texture of the film. Biaxial texture, which has a preferred crystallographic direction for both out-of-plane and in-plane directions, can decrease both twist and tilt misorientation between grains. One way to develop biaxial texture is application of an ion beam during the initial stages of nucleation of a thin film. This ion beam assisted deposition (IBAD) process uses a low energy (< 1keV), inert (Ar^+) ion beam to develop in-plane texture in a growing thin film during concurrent physical vapor deposition of the desired source material. The ion beam is aligned along a particular crystallographic direction at an oblique angle relative to the desired out-of-plane growth direction. The ion beam sputters away unfavorably oriented crystallites and allows favorably oriented crystallites to survive and grow. If the correct channeling angle is selected then bi-axial texture can be developed.

Background

The IBAD process has been used to form MgO template layers for seeding crystallographic texture in the high temperature superconductor $YBa_2Cu_3O_{7-\delta}$ (YBCO), as its superconducting properties are dependent upon the amount of in-plane alignment. Typically, IBAD MgO can be deposited with an in-plane texture of 5-6° phi-scan FWHM and an out-of-plane texture of 1-2° omega scan FWHM [4]. This texture develops in about 10 nm and the subsequent deposition of YBCO has a phi-scan FWHM of about 1°, which is very near single crystal quality.

Choi et al. used an IBAD MgO template layer, optimized for high-temperature superconductor coated conductors, as a template layer for the deposition of polycrystalline silicon [5]. Silicon films deposited on this template layer have reduced grain boundary misorientation and increased carrier mobility [6].

In our initial work, we use the IBAD process to develop a template layer for the subsequent deposition of polycrystalline silicon for photovoltaic applications. We chose CaF_2 as our starting template material because it fulfills some of the empirically accepted criteria for a good IBAD candidate material [7]. CaF_2 is a cubic material with well-defined channeling planes, is highly ionic in bond character, and CaF_2 is a good lattice match with Si with lattice parameters of 0.5451 nm and 0.5431 nm, respectively. In this report, we describe the development of IBAD CaF_2 as a template layer for the subsequent deposition of heteroepitaxial polycrystalline silicon with low angle grain boundaries associated with biaxial crystallographic texture.

Results From Initial Work

Four types of substrates were used in these experiments: fused silica; silicon (100) coated with 800 nm of thermally grown SiO_2; single crystal yttria-stabilized zirconia (YSZ) (111) or (100); or CaF_2 (111) or (100) single crystals. All substrates used in these experiments were nominally 1 x 1 cm in size.

Depositions for these experiments were performed in a PVD high vacuum system with a typically base pressure of 7.0×10^{-6} Pa (5.0×10^{-8} torr) at room temperature. A four-pocket 7 cc Temescal SuperSource provided the deposit vapor flux. A two-grid collimated Kaufman ion source at an incidence angle of either 35.3°, 45° or 54.7° (corresponding to particular crystallographic directions in the CaF_2 crystal) relative to the substrate normal provided an Ar ion flux to the substrate. The ion current density was monitored with a separate Faraday cup. The Faraday cup was biased at -20 V to eliminate contributions from electrons to the ion current reading.

The CaF_2 layer was deposited with concurrent Ar ion and CaF_2 fluxes. The ion energy range for these studies was varied between 200 and 900 eV with a current density of ~80 $\mu A/cm^2$. The electron beam evaporator provided the CaF_2 vapor flux at 0.06 nm/s to 0.11 nm/s. The flow rate of Ar gas into the system was kept constant at 10 sccm, which corresponded to a chamber pressure of $\sim 5.0 \times 10^{-3}$ Pa. Subsequent Ge and Si films were deposited in-situ using e- beam evaporation at 570°C and 0.05 nm/s. In some cases, the Ge and Si layers were sputter deposited at temperature between 500°C and 800°C.

The film growth was monitored in-situ using reflection high-energy electron diffraction (RHEED). The RHEED beam is aligned along an axis 90° relative to the ion beam. All patterns were taken at an electron beam energy of 28 keV.

The crystal structure of the films was determined ex-situ using X-ray diffraction (XRD). Samples were characterized for both in-plane and out-of-plane texture. Symmetric theta-2theta scans were used to verify that the desired phases were present in the deposited films.

To determine if texture could be developed in CaF_2 by IBAD processing we deposited CaF_2 IBAD films onto fused silica with a deposition rate of 0.06 nm/s and ion beam energy of 500 eV. The beam current density was ~80 $\mu A/cm^2$. The CaF_2 oriented with a (111)-type texture out-of-plane in ~10 nm of deposited film as shown in the RHEED image captured at the end of the IBAD run in the upper left of Figure 1. A subsequent 30 nm homoepitaxial layer of CaF_2 was deposited at 400°C and its in-plane texture was measured to be ~15° FWHM for the (220) in-plane peaks as shown in Figure 1. The RHEED diffraction spots increased in intensity and sharpened as the epitaxial CaF_2 layer was added indicating that texture improved from the initial IBAD layer. This behavior is similar to the improvement in texture observed for homoepitaxially deposited layers of MgO on IBAD [8].

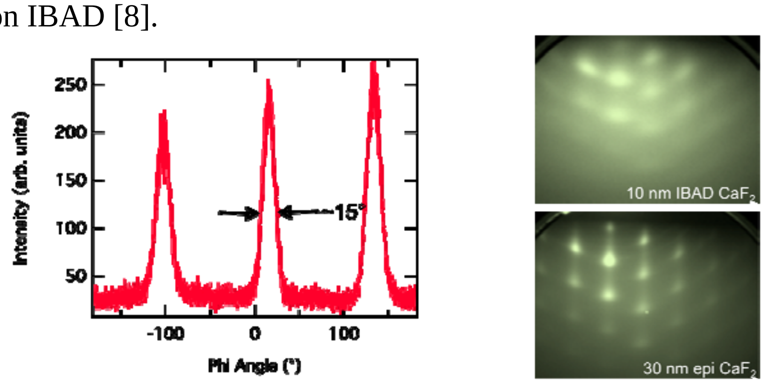


Figure 1. RHEED images and (220) phi scan for an IBAD CaF_2 film with a 30 nm homoepitaxial layer.

In a parallel effort to demonstrate proof-of-principle, we used single crystal substrates of (111) and (100) CaF_2 to determine if CaF_2 is a suitable seed layer for epitaxial growth of silicon. Preliminary results, however, were inconclusive. Little separation exists between CaF_2 and Si X-ray peaks and the CaF_2 single crystal substrate peaks were so intense that the Si peaks could not be easily distinguished using our standard laboratory X-ray diffraction methods. In order to reduce this diffraction interference, we used yttria-stabilized zirconia (YSZ) single crystal substrates capped with thin (30 nm) layer of CaF_2. The YSZ peaks are sufficiently removed from the Si peaks and the small X-ray diffraction signal from the thin CaF_2 layers will not swamp the signal from the thin Si films. The CaF_2 aligned well on YSZ (111) and (100) single crystal substrates, but silicon did not grow epitaxial on these capped single crystal seeds [9]. Ge, however, did grow epitaxially on the CaF_2/YSZ substrates, and provided an excellent seed for subsequent growth of Si [9]. Deposition of the Ge at 700°C produced an epitaxial layer with good (<1° FWHM) in-plane alignment as shown in Figure 2. The subsequent deposition of Si on this Ge-buffered substrate resulted in an epitaxial film as indicated by the spot pattern for the Si in the upper RHEED image in Figure 2. This high degree of orientation achieved indicates that growth of Si on textured CaF_2 proceeds with little-to-no degradation in crystallographic orientation.

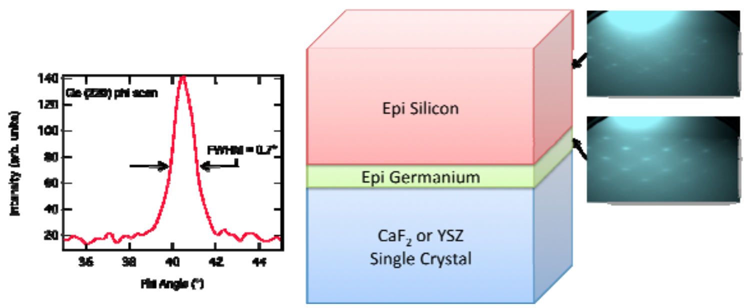


Figure 2. An illustration of the architecture used for the proof of principle experiments used to determine whether Si can be deposited on CaF_2. The XRD phi-scan on the left shows the epitaxial nature of the Ge layer deposited on CaF_2.

The final experiment was to assemble the IBAD CaF_2 film with the Ge buffer layer and silicon thin film as shown in the illustration in Figure 3. RHEED images taken at the conclusion of each deposition step are included in Figure 3. The IBAD CaF_2 was deposited to a thickness of 10 nm at room temperature. An additional epitaxial layer of CaF_2 was deposited to a thickness of 100 nm at a temperature of 400°C. A 50 nm thick epitaxial Ge layer was then deposited at 560°C. The final epitaxial Si layer was deposited to a thickness of 150 nm at 560°C. Note that the starting substrate RHEED image shows only a diffuse scattering from the amorphous oxide substrate. Thus the biaxial texture in the film layers is induced by the IBAD growth process rather than any influence from the starting substrate.

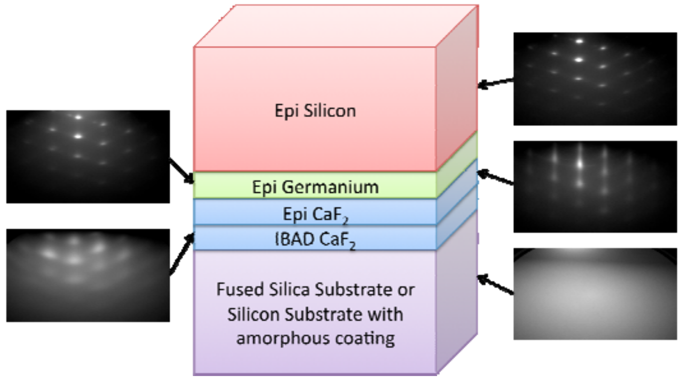


Figure 3. An illustration of the architecture used for the IBAD CaF_2-templated polycrystalline Si structure. The accompanying RHEED images were taken at the conclusion of each layer's growth.

The XRD analysis of the film structure described in Figure 3 showed the presence of good in-plane alignment throughout the film structure. We used the (220) peaks to characterize the in-plane texture for both the Si and CaF_2 films. As shown in Figure 4, the CaF_2 (220) peak had a full-width-at-half-maximum (FWHM) of 16.3° (with a 50 nm homoepitaxial CaF_2 layer). Deposition of the Si layer improves the texture by ~6° in-plane to a value of 10.8°, which indicates that the texture improves with each subsequent layer. This is similar to the improvement observed with homoepitaxial growth on IBAD seed layers [10]. This suggests that the texture is improved by grain growth competition and the overgrowth of misoriented grains, similar to that which is commonly observed in thin film microstrucutral evolution [11]. Further evidence of this effect is indicated in the sharpening of the RHEED image spots shown in Figure 3 for each additional layer.

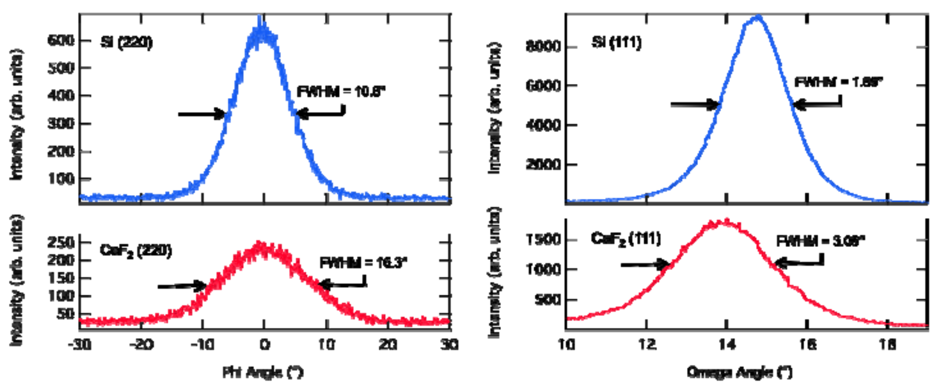


Figure 4. The XRD spectra of a film with the architecture illustrated in Figure 4. On the left are phi-scans of the CaF_2 (lower left) and Si (upper left) (220) peaks with FWHM of 16.3° and 10.8°, respectively. On the right-hand side are the omega (out-of-plane) scans for the (111) peaks of the two layers.

The films exhibit excellent out-of-plane alignment and no additional phases are detected as indicated by the theta-two theta XRD scan of Figure 5. Only the (111) reflections are observed for the Ge and Si films. Only two additional peaks are contributed to the scan by the substrate. The Si (111) most likely includes a contribution from the CaF_2 IBAD and homoepitaxial layers, but this is indistinguishable from the Si peak without the use of high-resolution optics and is the subject of a future investigation.

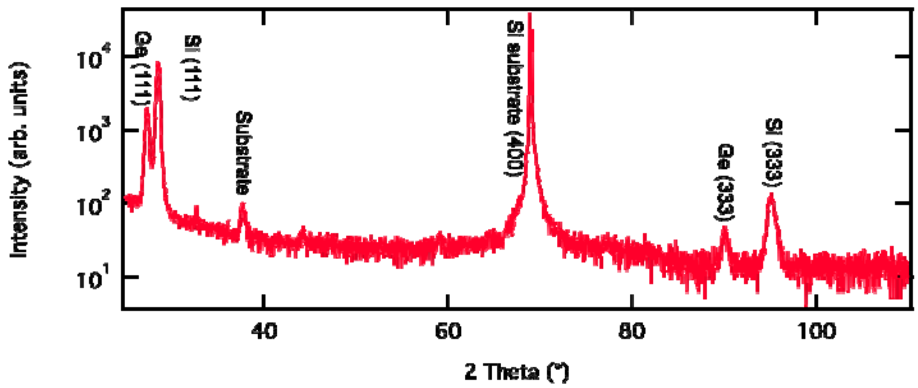


Figure 5. The theta-2 theta XRD scan for a Si (100) wafer with native oxide/IBAD CaF_2/epi CaF_2/30 nm Ge/150 nm Si.

Results From Recent Work

In recent work, improvement in the texture of our CaF_2 and Ge films has been achieved. Figure 6 shows CaF_2 having in-plane texture of 14.1° FWHM and out-of-plane texture of 3.34° FWHM. Ge exhibits in-plane texture of 5.04° FWHM and out-of-plane texture of 2.73°. These XRD patterns show that with the deposited Ge layer, the in-plane texture improves by ~9° and out-of-plane texture improves by ~0.6°.

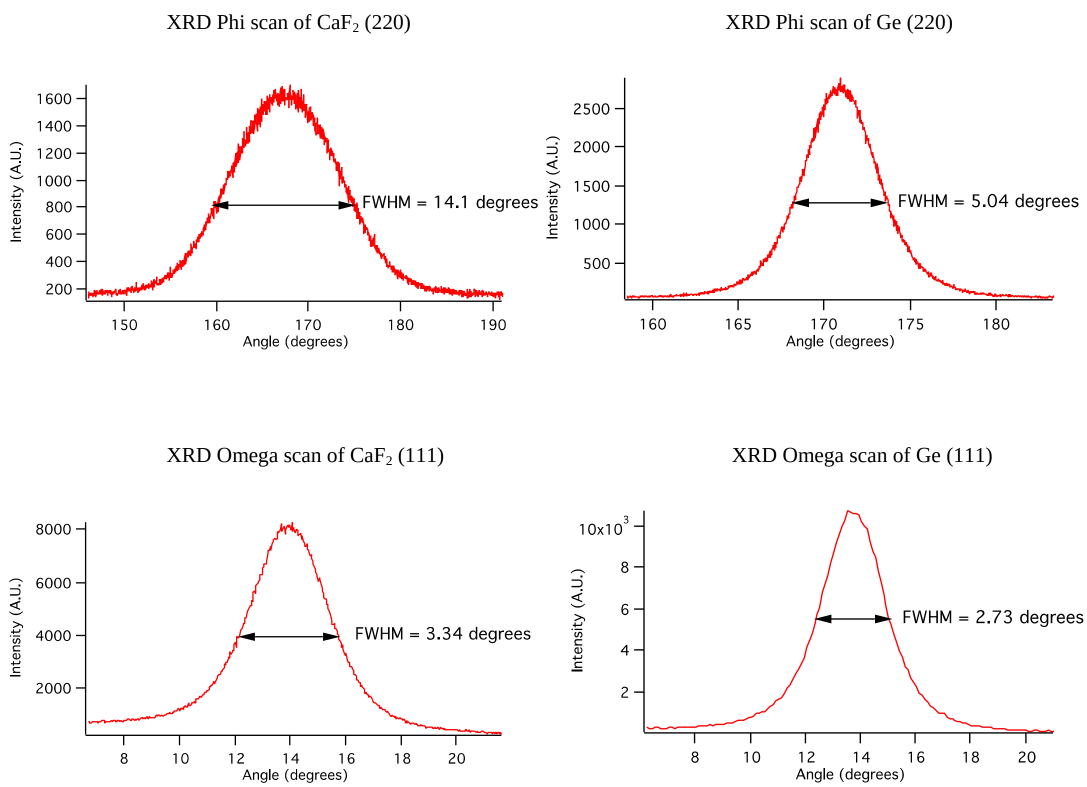
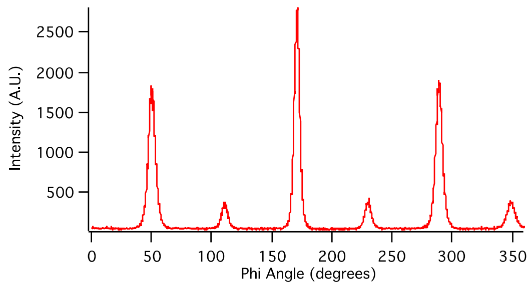


Figure 6. XRD Phi and Omega scans of CaF_2 and Ge films

In Figure 7, a full Phi Scan of Ge (220) reveals 6 peaks instead of the expected 3 peaks, which suggests the presence of twinning. Also from the pole figure of Ge in Figure 8, 3 strong peaks can be seen which indicate strong preferred grain orientation. The presence of several weaker peaks signifies twinning along the different [111] directions.



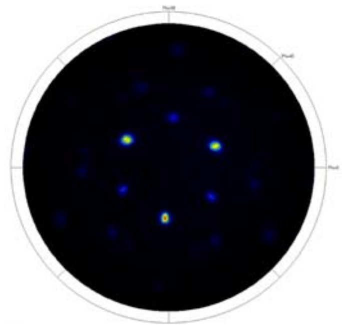
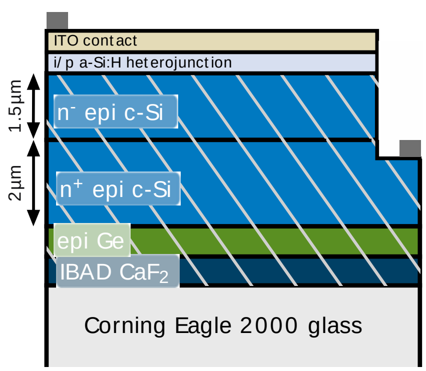


Figure 7. XRD Phi scan of Ge (220)

Figure 8. XRD Pole Figure of Ge film

In collaboration with National Renewable Energy Laboratory (NREL), our first solar cell has been fabricated with IBAD CaF_2 films from our initial work. The device structure is shown in Figure 9. Using the IBAD CaF_2/Ge template,[12] we grew a film silicon solar cell using hot-wire chemical vapor deposition (HWCVD).[13] The c-Si layer was hydrogenated at 610 °C and a *np* heterojunction was formed with a-Si:H. ITO was used for anti-reflection and the top contact.



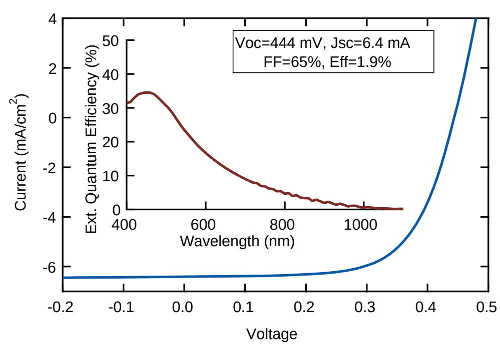


Figure 9. Solar Cell Device Structure

Figure 10. IV and EQE of our 1st solar cell

Figure 10 shows the EQE and IV characteristics of our solar cell. The 444 mV V_{oc} and quantum efficiency indicate that the diffusion length in the c-Si is smaller than the absorber thickness.[14] The J_{sc} is limited by the thin absorber and absence of light-trapping. The diffusion length will likely increase with improved grain orientation and optimized H passivation.

Conclusion

We have shown that CaF_2 is a suitable material for the IBAD process and useful as a template layer for subsequent germanium and silicon deposition.

The Ge films are well oriented with XRD measuring in-plane FWHM of ~5° and out-of-plane FWHM of ~2.7°. Initial test silicon solar cells were fabricated using epitaxial HWCVD. These devices yielded open circuit voltage of 444 mV which is higher than what would be achieved with similarly-fabricated un-oriented polycrystalline silicon. We expect our solar cell efficiency to improve in the future when we make devices with our improved textured films and incorporate light trapping techniques. This would be a step towards achieving a low-cost, high efficiency solar cell, which would greatly reduce the cost of PV and enable solar energy to be more competitive in the energy market.

Publications:

1. James R. Groves, Garrett J. Hayes, Joel B. Li, Raymond F. DePaula , Robert H. Hammond, Alberto Salleo and Bruce M. Clemens, "Biaxial Texturing of Inorganic Photovoltaic Thin Films Using Low Energy Ion Beam Irradiation During Growth" Materials Research Symposium Proceedings, Spring 2010.

References

1. M. A. Green, *Silicon Solar Cells: Advanced Principles and Practice*. (University of New South Wales, Sydney, NSW, Australia, 1995). L. Carnel, I. Gordon, D. van Gestel, G. eaucarne, J. Poortmans, A Stesmans, Journal of Applied Physics, 100, 063702 (2006).
2. C. A. Dimitriadis, Solid State Commun. **56** (11), 925 (1985).
3. W. Seifert, G. Morgenstern and M. Kittler, Semicond. Sci. Technol. **8** (9), 1687 (1993).
4. P. N. Arendt and S. R. Foltyn, MRS Bull. **29** (8), 543 (2004).
5. W. Choi, V. Matias, J. K. Lee and A. T. Findikoglu, Appl. Phys. Lett. **87** (15), 262111 (2005).
6. A. T. Findikoglu, W. Choi, V. Matias, T. G. Holesinger, Q. X. Jia and D. E. Peterson, Adv. Mater. **17** (12), 1527 (2005).
7. H. Matzke, Radiat Eff. Defects Solids **64** (1-4), 3 (1982).
8. J. R. Groves, P. C. Yashar, P. N. Arendt, R. F. DePaula, E. J. Peterson and M. R. Fitzsimmons, Physica C **355** (3-4), 293 (2001).
9. J. R. Groves, G. J. Hayes, J. B. Li, R. F. DePaula, R. H. Hammond, A. Salleo and B. M. Clemens, in *2010 MRS Spring Meeting* (San Francisco, CA, 2010).
10. S. Gsell, M. Schreck, R. Brescia, B. Stritzker, P. N. Arendt and J. R. Groves, Jpn. J. Appl. Phys. **47** (12), 8925 (2008).
11. M. Ohring, *Materials Science of Thin Films*, 2nd ed. (Academic Press, San Diego, CA, 2002).
12. C.W. Teplin et al, J. Non-Cryst. Sol.**352**, 984 (2006).
13. H.M. Branz et al, Thin Sol. Films (2011).
14. K. Alberi et al., Appl. Phys. Lett. 96, 073502 (2010).

Contacts

Bruce Clemens: bmc@stanford.edu
Alberto Salleo: asalleo@stanford.edu
Robert Hammond: rhammond@stanford.edu
Joel Li: joelli@stanford.edu
J. Randy Groves: jgroves@stanford.edu
Garrett Hayes: ghayes@stanford.edu