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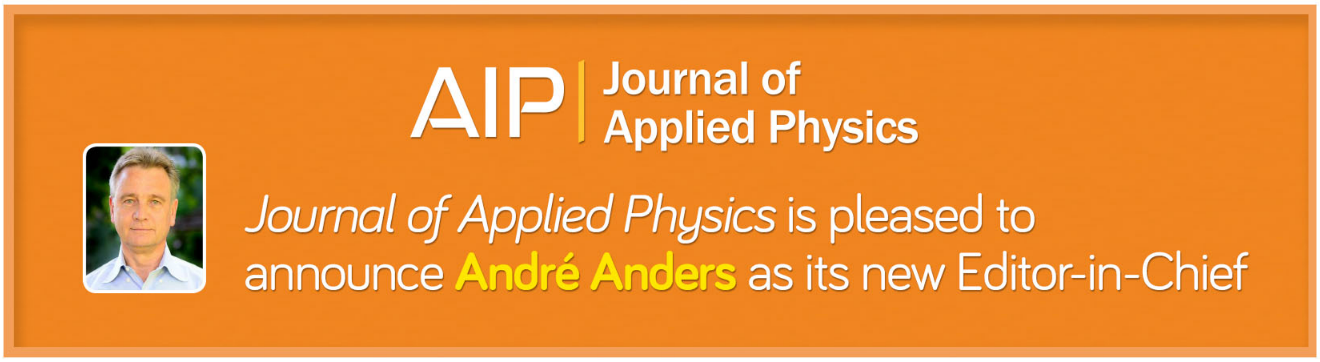

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High-efficiency heterojunction solar cells on crystalline germanium substrates

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We report stand-alone heterojunction (HJ) solar cells with conversion efficiencies of 5.9% and 7.2% on *n*-type and *p*-type crystalline germanium (c-Ge) substrates, respectively. The emitter of the HJ solar cells is formed by growing thin layers of highly doped hydrogenated microcrystalline silicon using plasma-enhanced chemical vapor deposition at temperatures close to 200 °C. The conversion efficiencies of the HJ solar cells are well-comparable with conventional devices fabricated at temperatures as high as 600 °C. We also study the surface passivation of c-Ge with hydrogenated amorphous and microcrystalline Si and correlate the passivation quality with the electrical performance of the HJ solar cells. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4737166]

Currently, the main application of crystalline germanium (c-Ge) in photovoltaics is serving as the bottom cell of high-efficiency multi-junction solar cells.[1,2] In these structures, c-Ge is the starting substrate, and the top cells which are comprised of III-V compound semiconductors are grown by epitaxial methods such as metal-organic chemical vapor deposition (MOCVD). The emitter junction of the c-Ge bottom cell is formed by the diffusion of phosphorous or arsenic into c-Ge during the growth of the top cell. Due to the current matching requirements of multi-junction solar cells and since in an optimum multi-junction solar cell design, only a small portion of the solar spectrum reaches the c-Ge bottom cell; the junction formation for the c-Ge bottom cell as described above is generally adequate and results in typical c-Ge bottom cell efficiencies of 2%–3%. However, a more sophisticated solar cell structure is required for stand-alone c-Ge solar cells in applications such as mechanical stacking where current matching requirements do not exist. Stand-alone c-Ge bottom cells with a conversion efficiency of 7.9% have been demonstrated for such applications and predicted to provide bottom cell efficiencies of 4%–5% in mechanically stacked multi-junction configuration.[3–5] Stand-alone c-Ge solar cells are also of interest for thermophotovoltaic applications.[5,6]

Stand-alone c-Ge solar cells demonstrated to date are formed by diffusion processes and require process temperatures close to 600 °C. Reducing the process temperature is desirable for lowering the thermal budget and therefore process cost and also for preserving the bulk lifetime of the c-Ge substrates. In addition, low process temperatures allow for applications in which thin layers of c-Ge are transferred from a host c-Ge substrate onto low-cost carrier substrates to reduce the high cost of the starting substrate. This is possible by a kerf-free layer transfer technique such as controlled spalling.[7] The narrow bandgap of the c-Ge bottom cell is suitable for various top cell structures such as p-i-n cells based on hydrogenated amorphous silicon (a-Si:H) and related alloys which are compatible with low-cost substrates due to their low-temperature growth. Since only a few microns of c-Ge is sufficient for current matching with the top cells in most thin-film technologies, the high cost of the c-Ge substrate is significantly reduced by multiple re-use of the c-Ge substrate.

Plasma-enhanced chemical vapor deposition (PECVD) of a-Si:H can produce high-quality films at low temperatures close to 200 °C and is a promising candidate for realizing high-efficiency heterojunction solar cells on crystalline substrates. The PECVD of *a*-Si:H is also appealing in that it is an established technology in large-scale production of thin-film transistor back-planes for active-matrix displays.[8] HJ solar cells have reached a conversion efficiency of 23.7% in the lab and 21.1% in production on crystalline silicon (c-Si) substrates.[9] Although a-Si:H has been used to passivate the emitter surface of c-Ge solar cells,[3–5] it has not been used to form heterojunctions on c-Ge substrates. In this letter, we study the surface passivation of c-Ge and show that hydrogenated microcrystalline silicon (μc-Si:H) provides a better surface passivation on c-Ge compared to that of a-Si:H. We also show that high-efficiency HJ solar cells can be achieved on c-Ge substrates by PECVD growth of amorphous and microcrystalline contact layers at temperatures close to 200 °C.

The schematic cross-section of the HJ solar cells on n-type and p-type c-Ge substrates is shown in Figs. 1(a) and 1(b), respectively. Substrate preparation includes cleaning and a final hydrogen termination step using a dilute hydrofluoric acid solution. The microcrystalline and amorphous layers are grown in a radio-frequency (13.56 MHz) multi-chamber PECVD reactor at temperatures close to 200 °C. A mixture of silane and hydrogen was used for the growth of intrinsic μc-Si:H and a-Si:H layers and *in situ* n-type and p-type doping was achieved by incorporating phosphine and diborane in the gas mixture, respectively. The substrate dependence of PECVD growth is well known, and at sufficiently high hydrogen dilution levels, silicon layers grown by PECVD may vary from fully amorphous to single-crystalline

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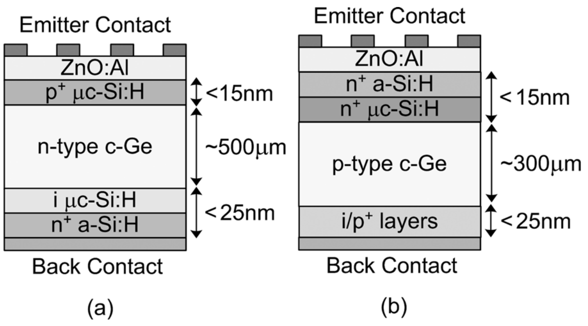

FIG. 1. Schematic cross-sections of the HJ solar cells fabricated on (a) n-type and (b) p-type c-Ge substrates.

depending on the substrate type.[10–13] We find that growth conditions that typically result in a-Si:H growth on amorphous substrates (such as silicon dioxide) and hydrogenated single-crystalline Si (c-Si:H) growth on c-Si substrates[12,13] result in μc-Si:H growth on c-Ge substrates. Al-doped zinc-oxide (ZnO:Al) was used as the transparent conductive electrode for the cells and was deposited by sputtering at room-temperature. The fabricated cells were annealed in dry nitrogen ambient to improve the emitter junction. The highest annealing temperature (which is the highest temperature used for processing the c-Ge cells) was close to 225 °C.

Passivation of c-Ge substrates by a-Si:H and μc-Si:H was investigated by microwave photoconductance decay (μ-PCD) using a SemiLab WT-2000PV tool with a 900 nm laser source. The effective minority carrier lifetimes were measured on 250 μm × 250 μm spots and averaged over a 500 mm × 500 mm area, i.e., 400 data points, with standard deviations below 5 μs. The effective minority carriers lifetimes measured on n-type and p-type c-Ge substrates coated symmetrically on both sides by ~50 nm thick a-Si:H or ~40 nm thick μc-Si:H layers are plotted in Fig. 2 for various annealing temperatures (the lifetime measured for as-deposited films is very close to that after annealing at 100 °C). It is observed that μc-Si:H provides a better surface passivation than a-Si:H on c-Ge, and the passivation quality improves by annealing at temperatures below (or close to) the PECVD growth temperature for both μc-Si:H and a-Si:H films. The improvement in surface passivation by annealing may be attributed to redistribution of hydrogen resulting in a higher hydrogen concentration at the c-Ge surface (Fig. 3). A higher density of hydrogen at the c-Ge surface is expected to saturate a larger density of Ge dangling bonds by forming Ge-H bonds, thus improving the surface passivation of c-Ge. At higher annealing temperatures, hydrogen is lost by outdiffusion from μc-Si:H and a-Si:H films and the passivation quality degrades. The degradation of lifetime occurs at temperatures higher than 225 °C and 250 °C for p-type and n-type c-Ge, respectively, and is more severe for p-type c-Ge. This is attributed to a stronger field-induced passivation in n-type c-Ge. Although the details of band alignment at the heterojunction depend on the spatial and energy distribution of defects in μc-Si:H and a-Si:H, a larger band-bending is expected in n-type c-Ge compared to p-type c-Ge due to the much larger valence band-offset, than the conduction band-offset, as shown schematically in Figs. 4(a) and 4(b). The strong electric field induced in n-type c-Ge shields the electrons from the n-type c-Ge surface and reduces the electron-hole recombination. As the films are annealed and the chemical component of passivation, i.e., H passivation of Ge dangling bonds is lost, the field-induced component of passivation remains in place and accounts for a lower degradation of passivation in n-type c-Ge compared to p-type c-Ge.

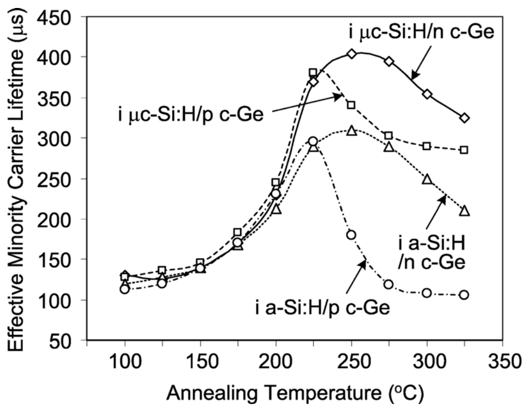

FIG. 2. Effective minority carrier lifetimes measured by μ-PCD on n-type and p-type c-Ge substrates passivated by intrinsic a-Si:H or μc-Si:H layer on both sides, as a function of annealing temperature. Annealing was performed in dry nitrogen ambient for 10 min.

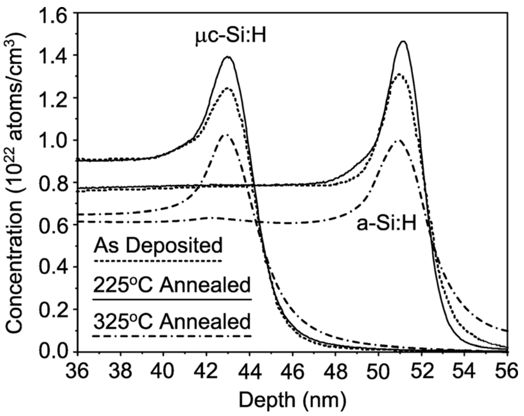

FIG. 3. Atomic concentration of hydrogen in ~50 nm thick a-Si:H and ~40 nm thick μc-Si:H films grown on p-type c-Ge substrates measured by secondary ion mass spectrometry (SIMS) for as-deposited films and films annealed at 225 °C or 325 °C for 10 min.

The quality of surface passivation has a direct impact on the performance of c-Ge solar cells. The evolution of the light I–V curves with annealing for a p-type c-Ge solar cell

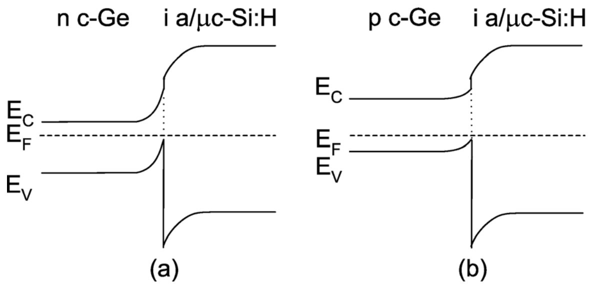

FIG. 4. Schematic energy band alignment at the heterojunction formed by a-Si:H or μc-Si:H on c-Ge for (a) n-type c-Ge and (b) p-type c-Ge substrates.

TABLE I. Comparison of the substrate properties and electrical characteristics of the HJ c-Ge solar cells presented in this work with the highest efficiency diffused-junction c-Ge cells (Ref. 5).

c-Ge Substrate properties				Cell characteristics			
Cell structure	Doping	Thickness	Resistivity	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	Efficiency (%)
HJ (This work)	n-type	~500 μm	0.1-0.4 Ω cm	221	48.1	55.6	5.9
HJ (This work)	p-type	~300 μm	0.2-0.4 Ω cm	248	46.6	62.1	7.2
Diffused (Ref. 5)	p-type	~170 μm	0.026 Ω cm	264	43.2	69.3	7.9

with an n^+ doped μc-Si:H/a-Si:H emitter stack as shown in Fig. 1(b) and aluminum back contact (i.e., no back surface field) is given in Fig. 5. In particular, the open circuit voltage of the cell is increased monotonically as the surface passivation is improved by annealing, and is a direct indication of a lower recombination rate at the emitter junction. The fill-factor of the solar cell is also improved by annealing, which is an indication of reduction in the density of interface states at the emitter junction. The so-called "S" shape of the light I–V curve at open circuit (i.e., $I = 0$) which has been also observed in c-Si HJ solar cells is believed to be due to the presence of interface states that distort the modulation of the Fermi level with the applied bias.[14,15] The observed "S" shape is suppressed by annealing and results in a significant improvement of the fill-factor, particularly at 225 °C (which is slightly higher than the PECVD growth temperature of 200 °C). Annealing at higher temperatures results in the degradation of the open circuit voltage (and also, but less significantly, the fill-factor) which result in the degradation of the solar cell conversion efficiency.

The conductivity of the μc-Si:H films was calculated from transmission line measurements and was found to be approximately 7.5 mΩ cm and 100 mΩ cm for best n^+ and p^+ films, respectively. High conductivity is essential for n^+ μc-Si:H films since the splitting of quasi-Fermi levels at the n^+ μc-Si:H/p c-Ge heterojunction is directly affected by the activated doping level in n^+ μc-Si:H. This is because the effect of conduction band-offset (expected to be lower than 0.2 eV) on the band-bending is low. However, the p^+ μc-Si:H/n c-Ge heterojunction is less sensitive to the activated doping in p^+ μc-Si:H, because the valence band offset (expected to be as large as 0.9 eV) has a larger contribution to the band bending. The open circuit voltage of p-type HJ c-Ge solar cells was found to slightly improve by adding an n^+ a-Si:H layer to the emitter stack. This is presumably due to a larger conduction band offset between a-Si:H and c-Ge, compared to that between μc-Si:H and c-Ge. However, we found that adding a p^+ a-Si:H layer at the emitter of the n-type HJ c-Ge cells severely degrades the fill-factor. This may be attributed to the suppression of hole tunneling due to the very large valence band offset between a-Si:H and c-Ge. For both n-type and p-type c-Ge cells, lateral carrier collection at the front metal grid is mainly dependent on the transparent conductive electrode (ZnO:Al), which has a sheet resistance of approximately 125 Ω/□.

The substrate properties and device characteristics of the HJ solar cells fabricated on n-type and p-type c-Ge substrates are listed in Table I and compared against the c-Ge cells fabricated by diffusion at temperatures close to 600 °C.[5] The conversion efficiencies of 5.9% and 7.2% achieved on *n*-type and *p*-type c-Ge substrates is close to the highest efficiency of 7.9% reported for the diffused cells (Fig. 6). We expect further improvement of the HJ c-Ge solar cell efficiencies by improving the PECVD growth conditions as well as the usage of more suitable c-Ge substrates. In particular, the open circuit voltage of the HJ cells is expected to improve with a higher c-Ge substrate doping and/or thinner c-Ge substrates.[4,5] A higher substrate doping increases the built-in potential at the emitter junction, while a thinner substrate reduces carrier recombination in the bulk, both resulting in lower dark currents and higher open circuit voltages.

In summary, we reported the fabrication of HJ solar cells with conversion efficiencies of 5.9% and 7.2% on n-type and p-type c-Ge substrates, respectively. The solar cell fabrication is enabled by PECVD growth of μc-Si:H and

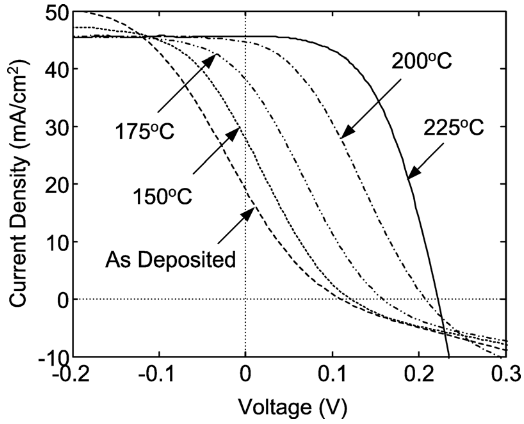

FIG. 5. Evolution of the light I–V curves of p-type c-Ge solar cells with n^+ doped a-Si:H/μc-Si:H emitter contact and aluminum back contact (no back surface field) as a function of annealing temperature.

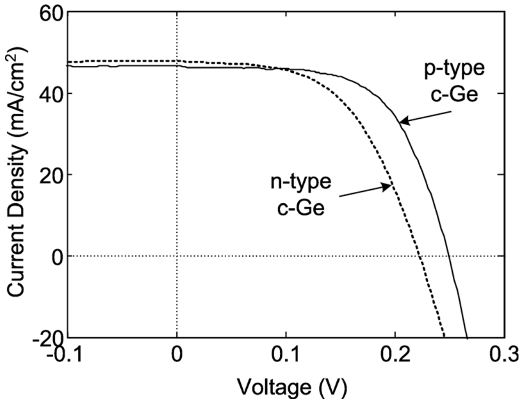

FIG. 6. Light I–V characteristics of the fabricated HJ solar cells showing conversion efficiencies of 5.9% and 7.2% under an intensity of 1 sun on n-type and p-type c-Ge substrates, respectively.

a-Si:H layers at temperatures close to 200 °C. The efficiencies of the HJ c-Ge solar cells are comparable with the efficiencies of conventional diffused c-Ge solar cells processed at temperatures up to 600 °C. We also studied the surface passivation of c-Ge with μc-Si:H and a-Si:H and showed that the passivation quality has a direct impact on the electrical characteristics of the HJ c-Ge solar cells.

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[1] D. C. Law, R. R. King, H. Yoon, M. J. Archer, A. Boca, C. M. Fetzer, S. Mesropian, T. Isshiki, M. Haddad, and K. M. Edmondson, Sol. Energy Mater. Sol. Cells **94**, 1314 (2010).
[2] R. R. King, D. Bhusari, D. Larrabee, X.-Q. Liu, E. Rehder, K. Edmondson, H. Cotal, R. K. Jones, J. H. Ermer, C. M. Fetzer, D. C. Law, and N. H. Karam, Proceedings of Prog. Photovoltaics in Proceedings of the 26th European Photovoltaic Solar Energy Conference, (Hamburg, Germany, 2011), p. 1.
[3] N. E. Posthuma, G. Flamand, and J. Poortmans, in 3rd World Conference on Photovoltaic Energy Conversion, Osaka, Japan, 11–18 May 2003, p. 777.
[4] N. E. Posthuma, J. van der Heide, G. Flamand, and J. Poortmans, IEEE Trans. Electron Devices **54**, 1210 (2007).
[5] J. vander Heide, N. E. Posthuma, G. Flamand, W. Geens, and J. Poortmans, Sol. Energy Mater. Sol. Cells **93**, 1810 (2009).
[6] J. van der Heide, N. E. Posthuma, G. Flamand, and J. Poortmans, AIP Conf. Proc. **890**, 129 (2007).
[7] S. W. Bedell, D. Shahrjerdi, B. Hekmatshoar, K. Fogel, P. Lauro, J. Ott, N. Sosa, and D. Sadana, "Kerf-less removal of Si, Ge and III–V layers by controlled spalling to enable low-cost PV technologies," IEEE J. Photovoltaics **2**(2), 141–147 (2012).
[8] B. Hekmatshoar, K. H. Cherenack, A. Z. Kattamis, S. Wagner, and J. C. Sturm, Appl. Phys. Lett. **93**, 032103 (2008).
[9] T. Kinoshita, D. Fujishima, A. Yano, A. Ogane, S. Tohoda, K. Matsuyama, Y. Nakamura, N. Tokuoka, Matsuyama, Y. Nakamura, N. Tokuoka, in Proceedings of the 26th European Photovoltaic Solar Energy Conference, Hamburg, Germany, 5–9 September 2011, p. 871.
[10] A. S. Ferlauto, R. J. Koval, C. R. Wronski, and R. W. Collins, Appl. Phys. Lett. **80**, 2666 (2002).
[11] P. R. Cabarrocas, N. Layadi, T. Heitz, B. Drevillon, and I. Solomon, Appl. Phys. Lett. **66**, 3609 (1995).
[12] D. Shahrjerdi, B. Hekmatshoar, S. W. Bedell, M. Hopstaken, and D. K. Sadana, J. Electron. Mater. **41**, 494 (2012).
[13] B. Hekmatshoar, D. Shahrjerdi, and D. K. Sadana, IEDM Tech. Digest **2011**, 36.6.1.
[14] M. W. M. Van Cleef, F. A. Rubinelli, J. K. Rath, and R. E. I. Schropp, J. Non-Cryst. Solids **227**, 1291 (1998).
[15] A. Froitzheim, K. Brendel, L. Elstner, W. Fuhs, K. Kliefoth, and M. Schmidt, J. Non-Cryst. Solids **299**, 663 (2002).