Multijunction Nanowire Solar Cells for Inexpensive and Highly Efficient Photoelectricity: Enabling Methods

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Abstract
During the 1st six months of this year-long GCEP Exploratory project, we have focused on preparation of highly textured (111)-oriented polycrystalline Ge films on glass substrates, as a method of producing inexpensive substrates for aligned nanowire or microwire photovoltaic device array deposition. We have demonstrated promising results on recrystallized amorphous Ge layers using Al-induced crystallization at moderate temperatures, and have grown nanowires on these poly-Ge template layers. We have also demonstrated Ge nanowire growth via Ni and Pd catalyst nanoparticles, although the resulting wire crystalline quality is poorer than that observed in Au-mediated vapor-liquid-solid (VLS) nanowire growth at comparably low temperatures.

Introduction
Solar cell technology is one of the most promising solutions for the global energy and greenhouse emissions problem. Despite its great potential, direct use of solar energy is currently only a minor component of the global energy system. The modest average solar energy flux at the surface of the earth (~200W/m²) sets severe requirements for the efficiency and cost of photovoltaic devices if they are to displace coal-fired electricity generation. Single-junction cells for the conversion of unconcentrated sunlight into electricity are limited by the Shockley-Queisser efficiency limit of 31%. [1] Higher efficiency can be achieved by state-of-the-art multijunction solar cells. This proposed exploratory research project will enable fundamental improvements in both efficiency and cost by use of multijunction photovoltaic devices based on single-crystal semiconductor NWs supported on inexpensive substrates.

Highly efficient two-junction cells based on single crystal III-V substrates were reported by Olson et al. in 1990. [2] The most efficient commercial photovoltaic cells today are 3-junction cells designed for use in space. They are fabricated from monolithic single-crystal III-V semiconductor layers on Ge single crystals. [3] Multijunction cells sequentially absorb different portions of the solar spectrum. When light absorption is properly balanced, the cells produce the maximum photocurrent with a photovoltage that is in principle equal to the sum of the photovoltages of the individual cells. Recent work has focused on initiation of epitaxy of the III-V materials on Ge [4] and on the important tunnel junctions required to provide Ohmic contacts between the n-doped side of one junction and the p-doped side of the next. [5] However, the single crystal substrates required to avoid carrier recombination at strain-induced dislocations make today’s multijunction cells too expensive for terrestrial application without concentration. The strategy in this project is to develop methods to use inexpensive glass substrates and inexpensively produced single crystal NW arrays to accomplish the same function at much lower cost.
The use of inorganic NWs is especially attractive because they can be grown with very high crystal quality at low temperatures of 250-500°C and promise many decades of durability under solar illumination. Figure 1 illustrates an eventual target, a 2-junction Ge/GaAs NW array. In comparison to monolithic multijunction solar cells, multijunction cells based on dense arrays of vertical NWs offer two distinct advantages: growth of single-crystal heterostructures on inexpensive amorphous substrates, and accommodation of misfit strains between different semiconductors by elastic dilatation, without formation of dislocations that promote carrier recombination. Misfit strains as great as 1% have been predicted to be fully accommodated without dislocation in NWs up to 200 nm in diameter. [13] To maximize the volume to surface area ratio of the nanowires, diameters in the several hundred nanometers to micrometer range will be explored.

In our previous work, [6] a strong preference for vertical Ge NW alignment was observed for <111>-oriented wires, which nucleate efficiently on Si (111) and Ge (111) surfaces. In order to avoid the need for single crystal substrates, this project will examine means of producing polycrystalline Ge template layers that exhibit a strong <111>-oriented texture to promote vertical <111>-directed NW nucleation and growth. Starting with inexpensive glass substrates, we will deposit amorphous Ge (a-Ge) films by low temperature CVD. An ultra-thin (10-50 nm) Al layer will be deposited on top of the amorphous semiconductor film. Following the reported work of He et al., [14] we will investigate post-deposition anneals at moderate temperatures (~250°C), which are reported to result in crystallization of the a-Si films, producing poly-Si films with a strong (111) crystallographic texture.
In the process, the initially-buried Si diffuses through the Al layer, so that the polycrystalline semiconductor film is present at the sample surface after crystallization. We are now studying this process for (111)-textured crystallization of a-Ge to produce vertical NW nucleation templates. Although Al-induced crystallization of (111)-oriented poly-Si has been demonstrated, the crystallization behavior of a-Ge is, at present, unknown. We will also investigate anneals to induce grain growth in the poly-Ge layers, thus reducing the density of carrier recombination centers. Doping the poly-Ge by \textit{in-situ} incorporation of impurities into the a-Ge film will be studied.

In addition to demonstration of textured (111) poly-Ge templates for epitaxial NW growth on inexpensive glass or metal substrates, we are also studying alternative catalysts to Au for low temperature nanowire and microwire growth. In addition to its high cost, Au is a problematic catalyst for growth of photovoltaic wire devices because it produces midgap states in Si and Ge which act as very efficient carrier recombination centers. We are investigating the kinetics and crystalline quality of Ge nanowire and microwire growth using Ni and Pd catalysts to determine the temperature and pressure limits within which long single crystal wires can be deposited.

**Results**

\textit{Growing Ge NW Arrays on (111)-Textured Polycrystalline Ge Thin Film Templates}

Vertical-aligned semiconductor nanowire (NW) arrays can be synthesized epitaxially on (111) single crystals [7, 9]. Ge NW-based photovoltaic devices could take advantage of the elastic dilatation property of nanowires that can relax misfit strains and allow the growth of high-quality nanowire heterojunctions with no dislocations. For such application, large-area low-cost substrates are needed to substitute expensive single crystal Si or Ge substrates. Here we report a processing technique to grow dense vertical Ge NW arrays on (111)-textured polycrystalline Ge thin films on inexpensive glass substrates.

As previously reported, metal-induced crystallization can obtain polycrystalline semiconductor thin films at moderate temperatures (~250°C), e.g., crystallization of amorphous Si (a-Si) layers by \textit{a-Si} diffusion through Al layers given Al/Si bi-layers deposited on glass substrates. Al/Si chemical composition exchange is expected after successful metal-induced crystallization, and is correlated with preferred (111)-oriented texture of crystallized Si thin films [8]. Initially, we duplicated the above structures in the Al/Ge system, by e-beam evaporating \textit{a-Ge} (100–150 nm) and crystalline Al (30–50 nm) thin films on fused silica substrates in sequence. X-ray photoelectron spectrum with sputtering was used to characterize the composition depth profile of as-deposited and annealed thin films. Fig. 2a shows the composition of as-deposited Al (50 nm)/\textit{a-Ge}(150 nm) bilayers on glass. Then, 250°C and 300°C annealing was carried out in a lamp-heated cold-wall reactor with 400 sccm H₂ flow and 5 Torr total pressure for 1 hour, respectively. The composition profile (Fig. 2b) indicates that significant Al/Ge inter-diffusion generally happened. The expected Al/Ge composition exchange was observed for 300°C anneals, because Ge’s diffusivity in Al is, in general, many orders of magnitude higher than the Al diffusivity in Ge [10, 11].
Figure 2: a) XPS composition depth profile of as-deposited Al/Ge bi-layers on glass. The chemical composition is calculated by Al 2p, Ge 3d, and O 1s peak intensities. b) Al/Ge composition depth profile after samples annealed at 250°C and 300°C, respectively.

Cross-section TEM characterization of the above samples suggests that Al-induced crystallization was uncontrolled, as shown in Fig. 3a. The light contrast regions in the Al/Ge layer are Al-rich crystallites, while the dark contrast regions are Ge crystallites, as confirmed by energy-dispersive spectrum (EDS). Clearly, more Al crystallites were distributed near the quartz surface, which is consistent with the previous observation. However, Ge layers are broken up into 10s’ of nm size crystallites, suggesting that obtaining quality (111)-textured polycrystalline Ge thin film from the uncontrolled Al-induced crystallization process is unlikely.

Figure 3: Cross-section TEM bright-field images of samples after Al-induced Ge crystallization, as well as the EDS analysis. a) Samples without a diffusion barrier after annealed at ~ 250°C. b) Samples with a diffusion barrier after annealed at 250°C for 1 hour. The inset table lists the EDS composition analysis of regions as indicated in b).

To control the diffusion process, we introduced a diffusion barrier between $a$-Ge and Al layers. The barrier was used to prevent the majority of $a$-Ge from directly contacting the Al layer during annealing, and thus forming 10s’ of nm-scale Ge crystallites. On the other hand, the barrier is thin enough to allow $a$-Ge to successfully diffuse through multiple defective sites in the barrier simultaneously, and promotes lateral Ge crystal overgrowth, thus forming a polycrystalline Ge layer on top of Al layer. Experimentally,
the diffusion barrier was created by intentionally oxidize as-deposited Ge layer in UV-O₃ for 3 minutes, prior to Al layer deposition. The sample was then annealed in UHV environment at 250°C for 1.5 hours after native Al₂O₃ removal. After annealing, the sample microstructure is shown in Fig. 3b, where a Ge overgrowth mechanism is obviously presented. X-ray diffraction (XRD) analysis in Fig. 4a shows the polycrystalline Ge has 75.1% texture enhancement on the (111) orientation, considering Ge (111), (220) and (311) are the only contributing peaks. Finally, we’ve grown vertically-aligned Ge NWs on this polycrystalline Ge film with (111) preferred-orientation, by a two-temperature VLS growth method [1, 2], as shown in Fig. 4b.

Figure 4: a) X-ray diffraction 2θ-ω symmetric scan of Al/Ge bi-layers with a diffusion barrier after 250°C anneals. b) 45° from plan view of Ge NW CVD growth on polycrystalline Ge films with (111) preferred-orientation. The inset shows Ge NWs with the same growth condition on a (111) single crystal Ge substrate.

Germanium Nanowire Growth using Electronically Benign Metal Catalysts

In the literature to date, growth of Ge nanowires has been reported by using Au as a catalyst. In most cases, the growth is said to have occurred by the VLS mechanism. Au has been a popular choice as a catalyst due to its chemical inertness and ability to form a eutectic with Ge resulting in nanowire growth at low temperatures. However, Au induces deep trap levels for charge carriers in Si and Ge. In order to make the Ge nanowires CMOS compatible and useful for photovoltaic applications, electronically benign metal catalyst is required. To begin with, Ni and Pd have been chosen as the potential electronically benign metal catalysts for Ge nanowire growth in this research project. Ni and Pd form eutectic alloys with Ge at much higher temperatures (762 and 725°C respectively) as compared to Au (363°C). Hence, the catalyst is expected to be in the solid phase in case of Ni and Pd catalyzed Ge nanowire growth below 500°C, which implies growth by the vapor-solid-solid (VSS) instead of the VLS mechanism.

Extensive studies of Au catalyzed Ge nanowires grown by CVD have shown that substrate surface orientation, growth temperature, partial pressure of precursor, total pressure in the reactor chamber etc. are key factors in determining the structure and properties of Ge nanowires. Hence, nanowire growth experiments were carried out by varying these growth conditions in systematic manner in order to obtain vertical nanowire growth on (111) oriented Ge substrate. Metal catalysts (Ni, Pd as well as Au for
comparison) were deposited on single crystal Ge substrate in the form of thin film by electron beam evaporation. Ge nanowires were grown in a cold walled CVD chamber with Germane (GeH₄) diluted with hydrogen as precursor gases. An annealing step was introduced prior to the growth in order to break the metal thin film into well defined nanoparticles. It was observed that Ni and Pd are indeed capable of catalyzing Ge nanowire growth but there is very little control over the structure of these nanowires as shown in the SEM images in Fig. 5. Figure 6 shows the TEM images of Ni and Pd catalyzed nanowires. It is believed that along with the growth conditions, it is necessary to study the interface between the catalyst particle and the substrate and its effect on nanowire growth.

Future work will involve the study of interaction between Ni and Pd catalysts and the substrate through annealing experiments. Use of different single crystal substrates with different orientations will give us further insight. We also wish to continue to experiment with the growth conditions like annealing temperature, growth temperature, partial pressure of precursor gases, total pressure etc. to achieve vertical nanowire growth with fewer twins and other defects. Once non-Au catalyzed CVD growth is optimized on single crystal substrates, we will transfer work on this process to the textured poly-Ge on glass substrates described in the previous section of this report.

**Figure 5:** SEM images of Ge nanowires grown using (a) Au, (b) Ni and (c) Pd as a catalyst on Ge(111) substrate at 450°C.

**Figure 6:** TEM images of (a) Ni and (b) Pd catalyzed Ge nanowires corresponding to SEM images in Fig 5.
References

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