Recrystallized Germanium on Ceramic for III-V Solar Cells Applications

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ABSTRACT

Germanium-on-ceramic substrates are developed for GaAs and other III-V compound semiconductor solar cell applications. Thin (2- to 5- micron) films of germanium are deposited on thermal-expansion matched polycrystalline alumina (Al_2O_3) substrates coated with a tungsten film that promotes wetting and adhesion. The Ge films are capped with various metal and oxide films, and then recrystallized in a rapid thermal processing (RTP) system. Average grain sizes greater than 1 mm are achieved. Epitaxial layers of GaAs epitaxy are grown on these structures using a close-spaced vapor transport (CSVT) technique.

1. Introduction and Background

The broad objective of this work is to combine the high performance of epitaxial III-V compound solar cells with the low-cost potential of polycrystalline solar cells deposited as thin-films on inexpensive substrates. This idea is not new, and efforts along these lines date from the 1970s. The early work and subsequent research gained some important results and insights, but also underscored various technical difficulties with this approach. Efficiencies were disappointing—usually in the range of 5 to 10% [1]—and this was attributed primarily to performance losses associated with the small grain size and unfavorable texture of poly-crystalline GaAs films deposited on dissimilar substrates such as metals, glass, graphite, fused silica, and ceramics. Grain boundary minority carrier recombination results in: i. poor collection of photogenerated carriers, thus reducing the short-circuit current; ii. increased junction reverse saturation currents, thereby lowering the open-circuit voltage; and iii. shunting effects, thus diminishing the fill factor. Grain boundary passivation was either not tried, or proved ineffective. Further, there was some concern that addressing these problems would add complexity and cost, and thus forego the advantages of a thin-film technology.

Since then, several new developments and continued progress in GaAs-based space cells make this approach increasingly attractive [2-6]. These include:

1. Epitaxial GaAs-based solar cells on GaAs and Ge single-crystal substrates have demonstrated some of the highest efficiencies (AM1.5) of any type of solar cell: GaInP/GaAs (30.3%, 4.0 cm^2), GaInP/GaAs/ Ge (31%, 0.25 cm^2 and 28.7%, 30 cm^2) [see www.pv.unsw.edu.au/eff for efficiency citations]. No doubt there will be performance penalties incurred upon applying these designs to polycrystalline materials. Nevertheless, these results suggest that if grain boundary losses can be adequately controlled, the efficiency of polycrystalline solar cells could well surpass 20%.
2. New proposed and modeled 4- and 5-junction tandem solar cell designs based on GaAs-related materials could have efficiencies approaching 40%. Clearly, the ultimate potential of III-V solar cells has not been exhausted.
3. GaAs solar cells grown by MOCVD on optical–grade polycrystalline Ge wafers have achieved efficiencies of about 20%, albeit with fairly sophisticated epitaxial device structures. The grain size of the Ge substrate wafer was approx. 1 mm.
4. GaAs solar cells made on single-crystal silicon substrates have also achieved efficiencies of 20%, which indicates that GaAs solar cells can be somewhat forgiving of stress and defects.
5. There is better understanding and more options for bulk and surface passivation of III-V semiconductors, although the effectiveness of these techniques for solar cells remains to be seen.

2. Criteria and Rationale

KURTZ and MCCONNELL [2] have assessed the materials and performance requirements for high-efficiency, potentially low-cost GaAs solar cells. Their criteria have guided our conceptualization and design of a GaAs-on-ceramic solar cell. At this stage of our work, we regard the grain size distribution as the most important metric of polycrystalline GaAs films for solar cells. The grain size required to reach 20% efficiency is a sensitive function of the degree of surface and grain boundary passivation, but a conservative estimate seems to be about 1 mm. This is corroborated by the demonstration of a ~20% efficient GaAs solar cell made on optical-grade polycrystalline Ge wafer with a 1-mm average grain size. Our basic idea is to develop an inexpensive surrogate Ge-on-ceramic substrate that will serve in place of such Ge wafer substrates. Subsequent work will utilize this new substrate in low-cost epitaxy processes, as well as investigate passivation techniques to improve performance, develop tandem cell designs, and implement series interconnection schemes for high-voltage monolithic module arrays.

For the near term, our baseline solar cell device is a *p-n* junction formed in GaAs epitaxial layer(s) grown on a Ge-on-ceramic substrate. The substrate is comprised of a large-grain (>1 mm) thin (~2 μm) Ge layer recrystallized on a tungsten-coated polycrystalline sintered alumina (Al_2O_3) ceramic. The rationale for this choice of materials is as follows. The alumina ceramic is made from inexpensive materials, is chemically inert, and has a high melting point. As indicated in FIGURE **1**, alumina also has a close thermal expansion match to Ge (and GaAs). This is useful to avoid thermal stress-induced defect generation and fracture or peeling of Ge films, and can be crucial if the Ge layer is melted and recrystallized, or subjected to other high-temperature processing steps. In general, silicon, Ge, GaAs and other III-V semiconductors deposited on dissimilar substrates typically exhibit grain sizes on the order of ~1 micron—probably too small for efficient photovoltaic devices. Recrystallization to enhance grain size turns out to be difficult for III-V compounds due to the volatility of Group V component (e.g., As) and non-stoichiometric melting. Silicon is difficult to recrystallize on account of its high melting point and reactivity, limited choice of compatible substrates, and the need for relatively thick solar cell layers. Ge may be unique among the established semiconductors as it is remarkably conducive to recrystallization and grain size enhancement. Moreover, Ge provides a good seeding surface for epitaxial growth of $Al_{1-x}Ga_xAs$ and $In_{0.5}Ga_{0.5}P$ due to its close lattice and thermal expansion match to these alloys. As implied by the results cited above, a high-efficiency *p-n* homojunction (or heterojunction) solar cell can be epitaxially grown on a Ge layer. Because the ceramic is insulating, an all-top-contact design must be used. On the other hand, an insulating substrate can be considered advantageous in facilitating isolation of array elements in monolithic series-interconnected modules. A number of surface passivating 'window' layers, such as wide-bandgap epilayers of AlGaAs, InGaP, or ZnSe, can be employed, as well as other encapsulating or passivation layers and/or surface passivation treatments. As a proof of concept, solar cells based on such GaAs / Ge /ceramic structures would validate the material quality and compatibility of materials combinations for such surrogate substrates, and serve as a starting point for more sophisticated tandem junction devices.

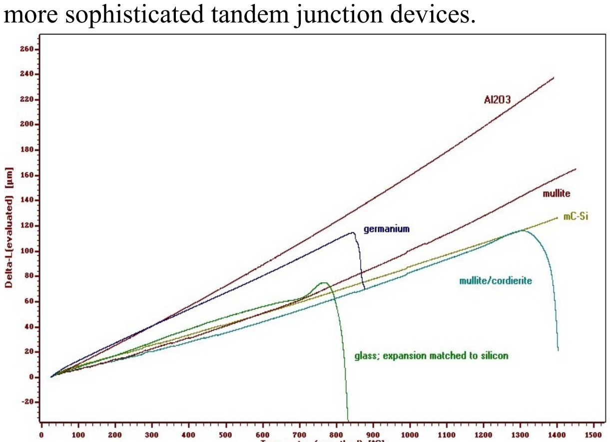

FIGURE **1**: *Thermal expansion of Ge and some candidate substrate materials.*

3. Methods and Results

Various alumina substrates are utilized including several commercial types from CoorsTek (Golden, Colorado), as well as alumina ceramic substrates made in-house using a tape casting process with 1-micron alumina particles in an organic solvent binder fired at 1500 ºC for three hours. There are minor differences in the optimum recrystallization conditions between different ceramics with different thicknesses, polishing, etc., but fortunately, a low-cost, unpolished tape-cast alumina ceramic produces good results. The ceramic is then coated with a 500-nm thick film of tungsten, which serves to promote wetting and adhesion of Ge during subsequent recrystallization. A 2- to 5-micron thick Ge layer is deposited on the tungsten-coated ceramic. Various capping layers of metals (e.g., tungsten, titanium, aluminum) and oxides are deposited on the Ge. All metal, oxide, and Ge layers are deposited by electron-beam evaporation, as this is most convenient for producing small batches of samples for experimental studies. SHINODA, OHMACHI and NISHIOKA [7,8] have described similar structures for GaAs/Ge-on-silicon LEDs. The Ge is recrystallized in a JIPELEC™ JetFirst Model ALU 100 Rapid Thermal Processing system by heating the sample to a peak temperature of 920 to 950 °C in 35 seconds, holding temperature for 10 s, and cooling at variable rates. The capping layers are then stripped by wet etching, after which the sample can be used for GaAs epitaxy. The variation of cooling rate during RTP recrystallization often reveals a trade-off between grain size (and texture) and voids formed in the Ge layer. The selection of capping layers and thicknesses of both the capping layers and Ge can completely eliminate the formation of voids. The capping layers may contribute to more favorable surface energetics and/or affect the heat transfer in the radiantly-heated RTP step. A detailed and systematic optimization study of the recrystallization is underway. Nevertheless, results to-date demonstrate the main initial objectives of the surrogate substrate approach have been met and the required substrate specifications with respect to grain size can be readily and reproducibly achieved. FIGURE **2** shows a top-view photomicrograph of a 2-cm x 2-cm sample with a 5-micron thick recrystallized Ge-on-ceramic layer. FIGURES **3** and **4** are top-views of samples that have been anisotropically wet etched to delineate grains (Fig **3**) and crystallographic orientation (Fig. **4**). We have made 1-cm x 1-cm samples in which the entire Ge layer has been recrystallized into essentially a single (111) oriented Ge crystal [6].

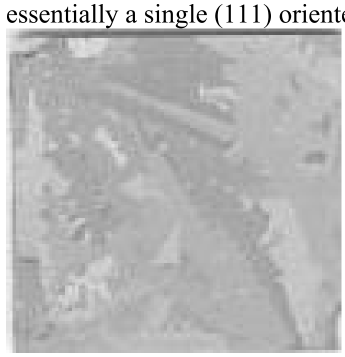

FIGURE **2**: *Top-view photomicrograph of 2-cm x 2-cm area of a recrysta-lized 5-µm thick Ge on alumina ceramic.*

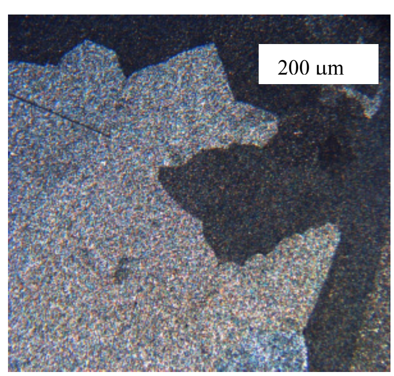

FIGURE **3**: *Sample similar to Fig.***2** *etched to reveal grain stru-cture.*

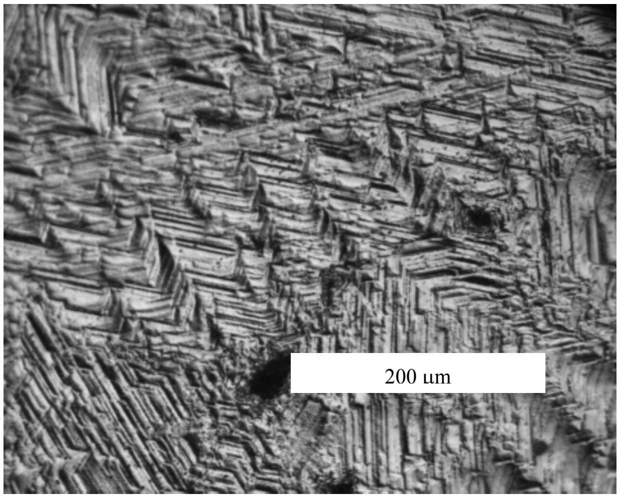

FIGURE **3**. *Anisotropically-wet etched recrystallized Ge-on-ceramic sample to reveal crystallographic orientation*.

The recrystallized Ge-on-ceramic layers have been successfully used as substrates for GaAs epitaxy. Currently, we use a simple close-spaced vapor transport (CSVT) technique [9] with water-vapor as a transport agent to grow a 2- to 10-micron thick epitaxial layer of GaAs.

As a variation of this process, the composite tungsten-Ge-capping layer films deposited on the ceramic are segmented by scribing down to the ceramic to form a rectangular array of 1-mm x 1-mm mesas. This patterned mesa array process is depicted in FIGURE **4** on the next page. Recrystallization can produce many single-crystal or twinned crystals of Ge, as shown in the photomicrographs of FIGURE **5**. These Ge islands have been used for selective GaAs epitaxy by CSVT.

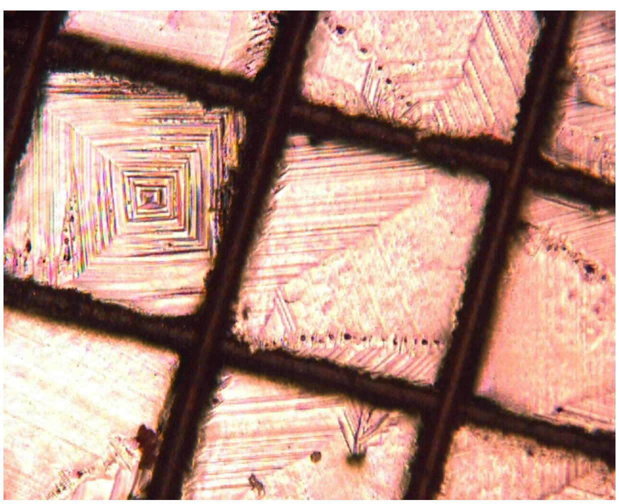
FIGURE **5a**. Patterned array of recrystallized 1-mm x 1-mm Ge-on-ceramic mesas.

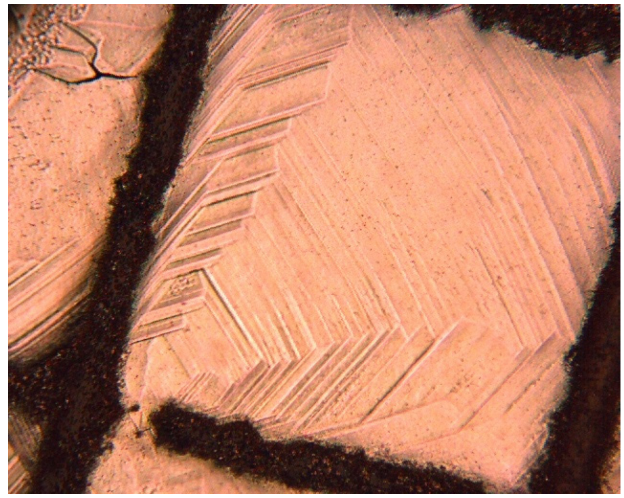
FIGURE **5b**.

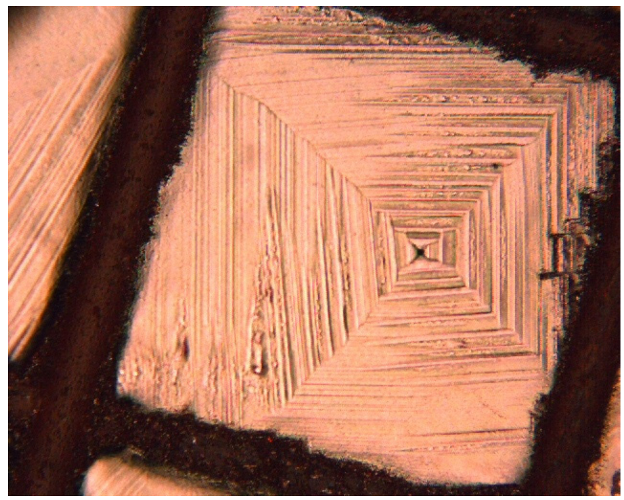
FIGURE **5c.**

4. Discussion and Conclusion

Large-grain (~1 mm) germanium films can be realized on thermal-expansion matched alumina ceramic substrates. These structures have been utilized for GaAs epitaxy using a simple close-spaced vapor transport technique. Ge cross-doping is a problem with the CSVT GaAs-on_Ge epitaxy [9], and therefore, other eptiaxy technologies, such as metalorganic chemical vapor deposition (MOCVD) may be better suited to grow the solar cell structures on the Ge-on-ceramic substrates.

A possible application of the process shown in Figure **4** is an array of solar cell mesas, which could be series-interconnected using printed metallization and/or transparent conductive oxides, possibly in combination with integrated microlenses or point focusing coverslips (see for example www.entechsolar.com). A potential advantage with such single-crystal 'islands' of GaAs/Ge is that grain boundary losses could be completely eliminated.

REFERENCES

[1] S.S. Chu, T.L. Chu, and H. Firouzi, "Thin-Film GaAs Solar Cells on Germanium-Coated Silicon Substrates by Chemical Vapor Deposition" *Solar Cells* **20** (1987) 237-243.

[2] S.R. Kurtz and R.McConnell, "Requirements for a 20%-Efficient Polycrystalline GaAs Solar Cell" *Future Generation Photovoltaic Technologies* R.D. McConnell, ed. AIP Conf Proc. **404** (1997) 191-205.

[3] R. Venkatasubramanian, E. Sivola, B. O'Quinn, B. Keyes, and R. Ahrenkiel, "Pathways to High-Efficiency GaAs Solar Cells on Low-Cost Substrates" ibid. 411-418.

[4] M.G. Mauk, B.W. Feyock, R.B. Hall, K. Dugan Cavanaugh, and J.E. Cotter, "Inexpensive Approach to III-V Epitaxy" ibid. 183-190.

[5] H.A. Atwater, J.C.M. Yang, and C.M. Chen, "Synthesis of Large-Grained Poly_Ge Templates by Selective Nucleation and Solid Phase Epitaxy for GaAs Solar Cells on Soda-Lime Glass" Ibid. 345-353.

[6] M.G. Mauk, J.E. Balliet, and B.W. Feyock, "Large-Grain (>1-mm), Recrystallized Germanium Films on Alumina, Fused Silica, Oxide-Coated Silicon Substrates for III-V Solar Cell Applications" to be published in *J. Crystal Growth*

[7] Y. Shinoda, T. Nishioka, and Y. Ohmachi, "GaAs Light Emitting Diodes Fabricated on SiO_2/Si Wafers" *Japanese J. Applied Physics* **22, 7** (1983) L450-L451.

[8] Y. Ohmachi, T. Nishioka, and Y. Shinoda, "Zone-Melting Germanium Film Crystallization with Tungsten Encapsulation" *Applied Physics Letters* **43, 10** (1983) 971-973.

[9] G. Lalande, N. Guelton, D. Cossemont, R.G. Saint-Jacques, and J.P. Dodelet, "Optimum Growth Conditions for the Epitaxy of GaAs on Ge by Close-Spaced Vapor Transport" *Canadian J. Physics* **72** (1994) 225-232.

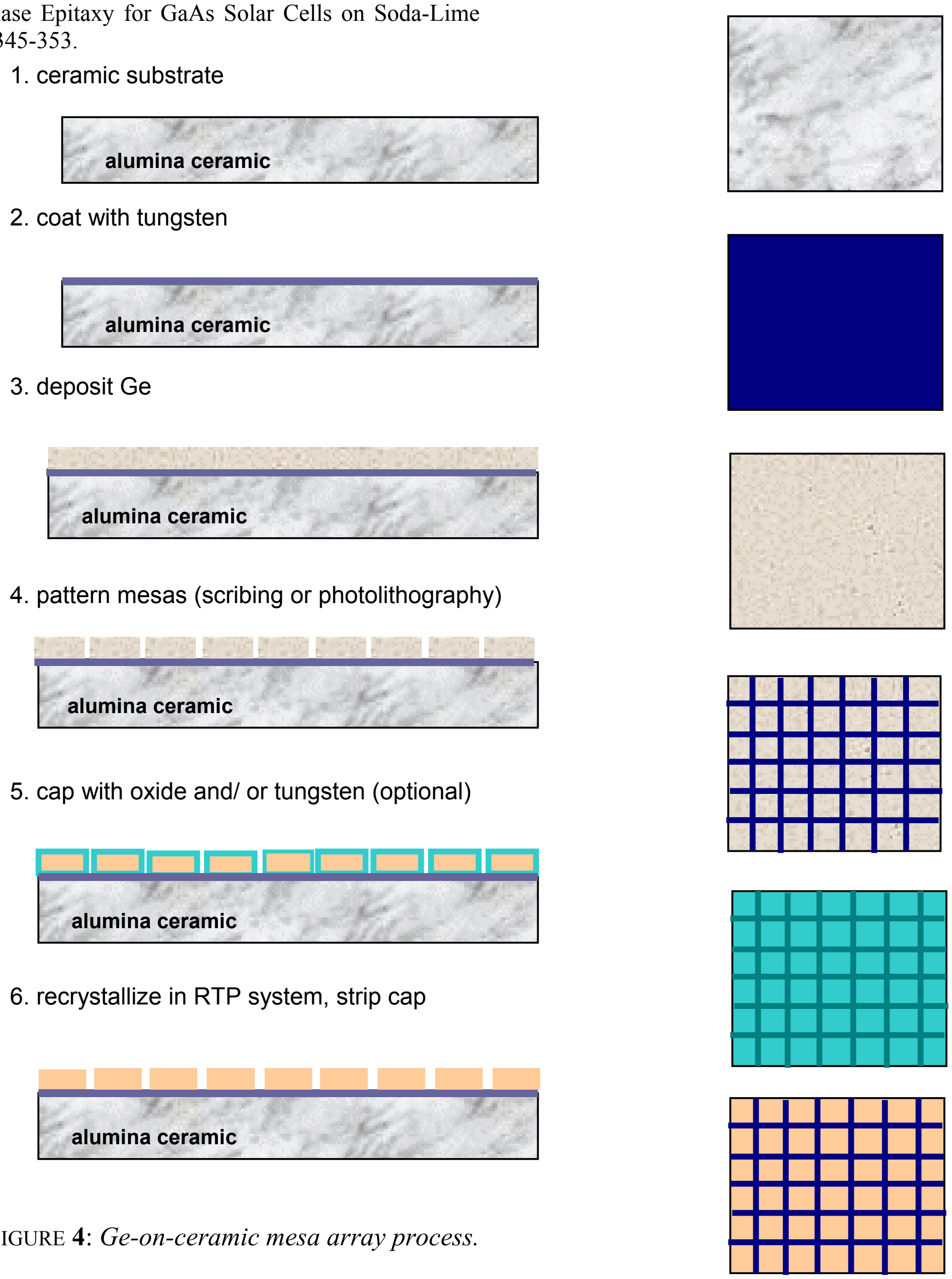

FIGURE **4**: *Ge-on-ceramic mesa array process.*