CRADA Final Report
for
CRADA Number ORNL93-0201

C. C. Klepper
Oak Ridge National Laboratory
Energy Conversion Devices

Approved for public release; distribution is unlimited.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
Abstract

This was a project that sought to improve the amorphous silicon-germanium (SiGe) thin film deposition process in the production of solar cells. To accomplish this, the electron cyclotron resonance (ECR) plasma discharge, employed for the thin film deposition, was be modified. Changes in the parameters of the plasma were monitored with diagnostic techniques, similar to those used in fusion plasma studies. That was the primary contribution from ECD. Only one phase was contained in the statement of work, with the following tasks: 1. Develop a detailed program for plasma characterization. This task was accomplished jointly. 2. Carry-out plasma modeling and analysis to support deposition systems design. This was also accomplished jointly by the partners. Several diagnostic systems were brought into operation and a few analysis algorithms were developed to handle the data. 3. Operate experimental deposition systems for the purpose of plasma characterization. This was the primary responsibility of ECD and was carried out in a satisfactory way. The facility was always available to joint experiments, whenever ORNL personnel visited the site. 4. Analyze data. This was a joint responsibility of the partners. Some data analysis was carried out remotely at ORNL. 5. Modify deposition as directed by measurements. This was primarily the responsibility of ECD. The flexibility that is characteristic of a small industrial laboratory allowed for frequent modifications to be carried out expeditiously, without significantly delaying the experimental program. One pattern disclosure resulted from the improvement of the microwave launcher in this facility. 6. This final report, which was deemed to be the only deliverable of this small project. And while the modified ECR discharge did not show measurable improvement of the conditions relevant to the deposition process, much was learned about the plasma parameters in the process. Some ideas on alternative designs are being discuss and funding options for testing such designed are being sought.

Technical Summary

The primary goal of this project was the explore the possibility of enhancing the efficiency of amorphous SiGe solar cells by improving the conditions under which Ge is deposited on the substrate. In particular, the modifications to the standard Electron Cyclotron Resonance (ECR) plasma processing reactor, proposed by ECD, would aim at increasing the temperature of the deposited species. This in turn would allow operation at lower substrate temperatures, which is desirable, since the presence of dangling bonds increases with the surface temperature. The intent was to use Ar in the discharges to validate the approach.
As mentioned above, an ECR configuration, most commonly used for plasma etching applications, was used in these studies. Such configuration involves a \(-1\text{kG}\) magnetic field and the electrons are heated by means of microwaves (MW) at the ECR resonance. One important aspect in the design of the plasma device the use of a windowless microwave launcher. This is especially important for deposition of non-dielectric materials (e.g. a-Si).

One of the problems that was encountered early on in the project was that the ECR plasma device was limited to operation at neutral pressures below 0.2 mTorr, due to breakdown in the launcher at higher pressures. A modification of the windowless MW launcher allowed increasing the pressure up to 1 mTorr and became the subject of a patent disclosure.

As with any study of plasma processes, it is important to determine the plasma parameters, such as the plasma potential ($V_p$), the electron temperature ($T_e$) and the electron or ion density ($n_e$ or $n_i$) and their spatial profiles. For such routine measurements, a Langmuir probe was employed. The cross-field dimension of the plasma is about 10 cm. The measured plasma potential was peaked on the axis and varied (spatially) from 35 to 45 V. The electron temperature varied from about 2 eV at the edge to 12 eV on axis. At 0.5 mTorr pressure, the ion density peaked at $8 \times 10^{11}$ cm$^{-3}$, which corresponds to at least a 5% ionization fraction.

A more challenging task was to determine a method for the measurement of the temperature of the ions and that of the neutrals. In fact, measurement of both species with the same technique was desirable. Optical Emission Spectroscopy (OES) was chosen for this task and was shown to be sufficient. An extant high-resolution monochromator (normally used for Raman spectroscopy) was equipped with a Peltier cooled photomultiplier tube, which was operated in the photon counting mode. The light was piped in from the plasma by means of a fiber optic cable, whose ends were shaped to image a circular spot at the center of the plasma onto the rectangular slit of the monochromator. A sheath polarizer was included in the collection optics to select the polarization. This was important because, at \(-1\text{kG}\) and at the low temperatures found for these species, the Zeeman splitting is comparable to the Doppler broadening, from which the temperature is deduced.

Even with the polarizer used to remove Zeeman components perpendicular to the magnetic field, a correction is needed to account for broadening due the relatively smaller splitting of the components parallel to the field. In addition, the instrumental broadening accounts for a substantial part of the measured broadening for low temperatures and needs to be deconvolved from the measured profile. In the process of analyzing these effects, the statistical factors that determine the precision of the measurements were determined.

The minimum uncertainty in the absolute values of the temperatures was determined to be about 100°C for the Ar neutrals and 150°C for the Ar ions. The small difference was only due to the fact that the ion lines were at lower wavelengths, where the instrument broadening was larger for the spectrometer used in these measurements. The key to achieving such high precision, for a measurement that is usually employed for temperatures above 10 eV, was the use of large numbers of measurements under similar conditions and the application of the rigorous statistical analysis, described in the attached copy of a paper submitted to the Journal of Vacuum Science and Technology.

As discussed in the paper, the ion temperature were found to be of the order of 0.5 eV. For the neutrals, a upper bound of 0.1 eV was set. This finding lays credence to the idea that the neutrals are very "cold" in plasma processing reactors and that it is reasonable to try to raise their temperature.
Inventions

As mentioned above, one patent disclosure was submitted during this project.

Commercialization

ECD has an excellent record of commercializing products that result of research and development. As indicated above, the research carried out on the deposition process did not show a conclusive improvement of the process. However, the measurements made have increased the understanding of the parameters that affect the process and may lay the ground for future work that would lead to improved products.

Future Collaboration

ECD has expressed an interest in further collaboration with ORNL. Thought is being given to a proper choice of direction for the research and to alternative funding opportunities.

Acknowledgments

This CRADA was supported by the U.S. Department of Energy under contact DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. (MMES) We acknowledge the valuable support from the MMES Office of Technology Transfer and the ORNL Office of Guest and User Services in the administration of the CRADA. We also acknowledge the support and encouragement throughout the project from ECD's president Stanford R. Ovshinsky.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL-73-0210: Final Report