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**CRADA Final Report
for
CRADA Number ORNL93-0201**

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Energy Conversion Devices

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**Final Report
for
CRADA No. ORNL93-0201
for**

Plasma Analysis and Diagnostics for High Efficiency Amorphous Solar Cell Production

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Abstract

This is 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 ORNL. 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 $\sim 1\text{kG}$ 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 10cm. The measured plasma potential was peaked on the axis and varied (spatially) from 35 to 45V. The electron temperature varied from about 2eV at the edge to 12eV on axis. At 0.5mTorr pressure, the ion density peaked at $8 \times 10^{11} \text{ cm}^{-3}$, 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 $\sim 1\text{kG}$ 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 10eV, 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 0.1eV 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 increase 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.

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