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I. Summary

The cryostat for in situ investigation of the optical and electrical properties of amorphous materials has been built and preliminary tests are now being made. This coupled with an ion pump vacuum system is expected to provide much needed information on the intrinsic nature of amorphous materials evaporated under controlled conditions. An optical system for measuring the incident, transmitted, and reflected beam is also completed and tested.

Work on the optical and electrical properties of amorphous silicon have been continued with improved precision. Optical measurement at the fundamental edge show that as in earlier measurements, the absorption edge shifts to higher energies as the annealing temperature is raised until about 400°C after which the edge is relatively insensitive to further anneal until crystallization. This behavior is attributed to the annealing of the defects in the amorphous states and is indicative of the existence of a well defined amorphous state. This is further supported by our recent observation that the electrical conductivity shows a similar insensitivity at about the same annealing temperature.

II. Research Program and Plan

In spite of a large number of investigations on amorphous semiconductors, a clear and consistent picture of the nature of the amorphous state in elemental semiconductors has yet to emerge. It is apparent that much of the results published in the literature are dependent on the techniques and apparatus used in the preparation of these amorphous materials. In an effort to establish these properties of amorphous materials which

are intrinsic to this state alone, a low temperature cryostat for in situ evaporation and measurement of amorphous materials has been constructed. The oil free vacuum system is capable of reaching at least 10^{-9} torr at room temperature. With a substrate holder whose temperature can be varied from 2°K up to 700°K and which is surrounded by low temperature shields, amorphous samples with a minimum of gas contamination can be produced and its electrical and optical properties immediately measured. These measurements include a.c. and d.c. conductivity, optical transmission and absorption both static and modulated, photomobility, photoconductivity and fluorescence.

Because of the very clean conditions prevalent, we wish also to introduce various gases into the system to observe their effect on the above measurements as well as on the structural properties of the material. The structural measurements (which can not be done in situ) would be made using the electron microscope, electron diffraction and X-ray diffraction.

III: Progress During Period

1. In situ measurements

(a) The cryostat for in situ measurement has been built and preliminary tests are being run.

(b) An ultra-high vacuum system has been assembled for pumping the cryostat and is in operation with a vacuum in the low 10^{-9} torr range.

(c) The optics for making the measurements described in section II is completed and spectra have been obtained on a variety of trial samples.

(d) The electronics necessary for both the optics and electrical measurements is complete and tested.

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2. Electrical and Optical Properties of Amorphous Silicon

Our studies of amorphous silicon in the past 6 months have been concentrated in two main areas. First, we wish to confirm our previous findings that the room temperature optical absorption is a function of annealing temperature up to anneals of $\sim 400^{\circ}\text{C}$ but relatively insensitive to anneals thereafter up to about 600°C . Recrystallization occurs on annealing between 640 and 700°C and the optical properties are characteristic of crystalline silicon.

Secondly, in view of the uncertainty in the functional form of the temperature dependence of the d.c. conductivity, we have undertaken the most precise measurements to date. We have calibrated a copper-constantan thermocouple to about $\pm .1^{\circ}\text{K}$. Also, we have switched to crystalline sapphire substrates for the increased thermal conductivity at low temperatures. Finally, we have used high value ($10^7\Omega - 10^{11}\Omega$) 1% resistors to calibrate a Keithley 601 Electrometer. Thus we have been making resistance measurements to 1% accuracy. Although it is the low temperature ($80\text{K} \lesssim T \lesssim 300\text{K}$) regions of conductivity with low activation energy for conduction that is the most interesting from a theoretical viewpoint,¹ we feel that the high temperature ($300\text{K} \lesssim T \lesssim 500\text{K}$) region must be covered so that the component of intrinsic conductivity can be measured and its contribution in the low temperature region accounted for. Thus the mechanism of low temperature conductivity can be clearly separated from the intrinsic conductivity. Recent work has failed to take account

1. Adler, D. CRC Critical Reviews in Solid State Sciences, Oct. 1970.

of this influence of intrinsic conductivity at the lower temperatures. Finally, a temperature stabilizing system has been built so that the temperature can be held constant while the conductivity is measured.

Although the electrical data has been taken, it is not yet fully analyzed. Analysis of the optical data, however, gives the same behavior observed in our earlier measurements, viz. the room temperature curve of $\alpha(\text{cm}^{-1})$ vs $h\nu$ shifts to higher energies with increasing anneal until about 400°C anneal. Thereafter, the movement of the $\alpha(\text{cm}^{-1})$ vs $h\nu$ curve is small with increasing anneal until 600°C anneal. The analysis of the electrical data is more difficult. A computer program to fit the data to

$$\sigma = \sigma_1 e^{-\left(\frac{T_1}{T}\right)^{N_1}} + \sigma_2 e^{-\left(\frac{T_2}{T}\right)^{N_2}}$$

is being written. The motivation for this form is furnished by the onset of intrinsic conductivity at high temperature and Mott's supposed $\ln \sigma \propto \left(\frac{1}{T}\right)^{1/4}$ relation at low temperatures for hopping within the localized levels.

Preliminary analysis of the electrical data does suggest some insensitivity of the conductivity between 400° and 600°C which may correlate with the optical data.