OPTICAL PROPERTIES OF AMORPHOUS GERMANIUM FILMS PREPARED BY CVD

D. D. Allred and J. A. Piontkowski
Energy Conversion Devices
1675 West Maple Road
Troy, Michigan 48084

EXTENDED ABSTRACT

The optical properties and the structure of amorphous germanium films have been the subject of numerous investigations in recent years [1-4]. These studies have indicated that the properties of the amorphous film depend on the deposition conditions and the thermal history of the samples. The methods of preparation most commonly utilized include vacuum evaporation[2] and sputtering[3] of germanium and the glow discharge decomposition of germane[4]. The fabrication of amorphous germanium films by chemical vapor deposition (CVD) has received less attention, perhaps the pyrolytic decomposition of germane is commonly performed in a temperature range that results in a polycrystalline film. For example, Powell states that germanium can be deposited by the pyrolysis of germane at beginning temperatures from 773 to 1073 K[5].

We have investigated the pyrolysis of germane below this range (625 to 735 K) in a hot wall low pressure CVD reactor. A carrier flow of 10% in H_2 in N_2 was utilized. The germane gas flow amounted to 22% of the total flow.

At deposition temperatures below 660 K the pyrolytic decomposition of germane results in an amorphous film as indicated by X-ray diffraction (XRD) patterns and variations in the absorption edge. At $T_s \leq 660$ K, all films appear amorphous by XRD but some, as Raman scattering shows, contain crystalline nuclei at the film substrate interface.. Between 660 K and 685 K the films are structurally inhomogeneous, changing from amorphous to completely polycrystalline as T_s increases. For $T_s = 675$ K the average particle size is, from XRD, 152 $\pm$ 20 Å, while it reaches 400-500 Å for the range 685 to 700 K. The polycrystalline films exhibit a pronounced (110) preferred orientation. Grains with the (100) orientation appear entirely absent and there appears to be about an order of magnitude fewer grains with the (111) orientation than expected if the orientation were random.

No impurities were detected by Auger or infrared absorption in films prepared at $T_s > 625$ K. From the sensitivity limits of the procedure, one concludes that the films contain less than 0.2 at.% of impurities heavier than hydrogen and less than 1.0 at.% hydrogen. It was determined that deposition rate (R) is activated over the entire temperature range studied, the activation energy being 28 Kcal/mole and is the same for amorphous and crystalline films.

Optical and electrical measurements compliment the X-ray results. Within the experimental error, the absorption coefficient profiles of the CVD samples prepared below 675 K are identical. Profiles of samples prepared at 685 K are intermediate to the 673 and 700 K profiles. The absorption coefficient profiles samples prepared above 700 K again resemble each other. Below 1.5 eV the refractive index for all CVD Ge samples, crystalline or amorphous, are within 5% of each other. From Tauc's plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$, the value of the optical gap, E_{oc}, is calculated to be (1.05 ± 0.05) eV for CVD a-Ge. The electrical conductivity of the amorphous films ($T_s \leq 660$ K) depends weakly on temperature and increases by only a factor of three as the temperature is increased from 630 to 675 K. Between 675 and 685 K the conductivity rises by approximately three orders of magnitude as the crystallites make contact with one another. The electrical properties of CVD a-Ge indicate that it probably possesses a large number of defects and states in the gap.

The amorphous films are very smooth; the polycrystalline films, however, become increasingly nonspecular with increasing T_s and thickness. Films deposited at $T_s = 675$ K become noticeably hazy for thicknesses greater than 3 μm. Whereas, films deposited at $T_s = 735$ K appear very milky for thickness as small as 1 μm.

In the present investigation we were also interested in thermal stability of the film properties and the kinetics of the crystallization process, since for some applications the temperature dependence of germanium's properties is important. We monitored changes in the optical reflectance, the optical transmittance, the X-ray diffraction and the film thickness of several CVD amorphous Ge annealed at 600 K as a function of annealing time. The results of this investigation show first, that CVD germanium films prepared below 650 K have optical properties similar to evaporated or sputtered germanium deposited at, or exposed to post deposition high temperatures. That is, they are in the anneal-stable amorphous state. It is also observed that films deposited between 650 to 675 K, while containing some crystallites, are substantially amorphous (> 98% of their volume).

It is also observed that the films eventually crystallize during anneal. The kinetics of crystallization of CVD germanium at 650 K can be described using the Avrami formula,

$$x = A\,[1-\exp\,(-t/t_o)^{-m}]$$

where x is the fraction of the volume crystallized and A is a proportionality constant. The coefficient m has the value of 5 when the sample is entirely amorphous (T_s = 650 K) and between 3 and 4 when it contains crystalline nuclei (T_s = 660 K). The characteristic crystallization time, t_o at T_a = 650 K is about 640 and 390 minutes for T_s = 650 and 660 K, respectively.

The deposition and annealing characteristics of these films parallel the characteristics of silicon films investigated by Janai, et al.[6], which were prepared by the pyrolysis of silane, except the characteristic temperatures for germanium are about 275°C lower than those for silicon.

The stability of the material against crystallization and oxidation is sufficient to warrant its use in solar absorbers used at 550°K. Its oxidation stability is promising at these temperatures and its optical properties are adequate to justify its trial in selective absorber applications and model studies.

REFERENCES

1. M.L. Theye, "Structural Effects in Tetrahedrally Bonded Amorphous Semiconductors" in: Optical Properties of Solids - New Developments, ed. B.O. Seraphin (North Holland, Amsterdam, 1976) ch. 7.

2. A.H. Clark, Physical Review, 154 (1967) 750.

3. G.A.N. Connell, R.J. Tempkin and W. Paul, Adv. in Physics 22 (1973) 643. See also other articles by the same group of authors, pages 531-642.

4. R.C. Chittick, J of Non Cryst. Solids, 3 (1970) 255.

5. C.F. Powell, J.H. Oxley and J.M. Blocker, Jr. Vapor Deposition (The Electrochemical Society, Inc. and John Wiley and Sons, Inc., 1966) p. 298.

6. M. Janai, D.D. Allred, D.C. Booth and B.O. Seraphin, Solar Energy Mat., 1 (1979) 11.

0214r