OPTICAL ABSORPTION AND STRUCTURAL ORDER IN SPUTTERED AMORPHOUS PHOSPHORUS

R. Pomian, L. Pilione, J. Lannin

To cite this version:

HAL Id: jpa-00220818
https://hal.archives-ouvertes.fr/jpa-00220818
Submitted on 1 Jan 1981

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
OPTICAL ABSORPTION AND STRUCTURAL ORDER IN SPUTTERED AMORPHOUS PHOSPHORUS

R.J. Pomian, L.J. Pilione and J.S. Lannin

Department of Physics, The Pennsylvania State University, University Park, PA 16802, U.S.A.

Abstract.-Optical absorption measurements are reported for rf sputtered a-P films prepared under conditions of variable substrate temperature. Variations in the optical gap with $T_s$ are similar to changes in the Raman scattering and x-ray diffraction spectra. The results suggest that intermediate-range order plays an important role for the structural, vibrational and optical properties for more ordered a-P films. Photostructural effects in As-chalcogenides which exhibit analogous behavior also suggest modifications of intermediate-range order.

Introduction.-Recent studies in thin film a-P have emphasized that intrinsic variations in network structure may arise with deposition conditions. Both Raman scattering and low-angle x-ray diffraction measurements suggest that static and dynamic correlation effects are present as a consequence of intermediate-range order, i.e., order beyond the first coordination shell $(1,2)$. Given these structural and vibrational results it is of interest to inquire if the electronic states of a-P are also influenced by structural correlations of intermediate range. In contrast to structural and vibrational probes, optical absorption measurements are more difficult to associate with structural modifications. In addition, extrinsic effects associated with voids or microstructure in general, may also play a role that requires consideration. In the present study we focus on modifications of the optical spectra in the near gap region on sputtered a-P films prepared under conditions of relatively high order as deduced from Raman scattering and x-ray diffraction measurements. The influence of short-range order and film morphology on the optical spectra will be presented elsewhere. The results discussed below suggest that in ordered a-P films intermediate-range order also modifies the electronic states via structural correlation effects. The absorption spectra also indicate that the Urbach slope is not sensitive to intermediate-range order, but may, in contrast to earlier suggestions $(3)$ vary in elemental semiconductors of similar coordination.

Experiment.-To systematically study variations in the physical properties of a-P films the rf plasma deposition conditions in a planar diode sputtering system were fixed and only the substrate temperature modified. The temperature of the films was determined directly by a thin film Ag-A1 thermocouple. An Ar pressure of 60 $\mu$ and a cathode-anode separation of $2''$ were employed to thermalize the incident P species and yield ordered films. The target employed was a $2''$ diameter piece of polycrystalline black P. Reflectance and transmittance measurements were performed on a Cary 14 system for 0.5-15 $\mu$ thick films. The absorption coefficient and index of refraction were determined by solving the appropriate film plus substrate equations $(4)$ using a microcomputer.

Results and Discussion.-In Fig. 1 the optical absorption coefficient of sputtered a-P films deposited at different substrate temperatures, $T_s$, is shown. The values of $T_s = 8, 64, 126$ and $180$ C for films A, B, C and D, respectively, were chosen to yield approximately $60$ C intervals in $T_s$. Although Fig. 1 indicates a relatively similar form for each of the films, the shift of the absorption spectra are clearly nonlinear in $T_s$. 

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphyscol:19814191
Figure 1 also indicates, with the exception of a small degree of tailing below ~1.7 eV, an exponential absorption edge whose Urbach parameter, $\Gamma$, has a relatively constant value of $8.2 \pm 0.8$ eV$^{-1}$. This value is approximately 30% lower than that of bulk a-As of 11.9 eV$^{-1}$ (3). Previous observations in elemental amorphous semiconductors have led some observers to suggest that the Urbach edge is primarily a function of coordination number (3,5). The results in a-P as well as recent measurements (6) in liquid (1-) S which indicate an Urbach parameter which differs considerably from that of a-Se and a-Te imply that other factors, such as the degree of covalency, may substantially modify $\Gamma$. The smaller value of $\Gamma$ in a-P relative to a-As implies a larger activation energy for electron delocalization in a-P. The relative constancy of $\Gamma$ with $T_S$ for the a-P films studied here contrasts with changes in the Raman scattering and low-angle x-ray diffraction spectra which indicate increasing disorder at lower $T_S$ values. A similar result is observed in 1-S, where $\Gamma$ is essentially independent of $T_S$ across the temperature range that includes the polymerization transition (6). The results in a-P and 1-S suggest that $\Gamma$ may be insensitive to longer range structural correlations and is primarily a function of short-range order. Considerable similarity in the Raman spectra of bulk a-P and the high $T_S = 180$ C film further predict comparable values of $\Gamma$ and $E_0$ for the bulk material. Microscopic inhomogeneities in bulk a-P samples examined to date have, however, prevented confirmation of this point.

The optical gap for the films of Fig. 1 have been determined by the conventional $(\alpha h \nu)^{1/2}$ vs. $h \nu$ plot shown in Fig. 2. The extrapolated $E_0(T_S)$ values are shown in Fig. 3, where the solid line is merely to indicate the trend at high $T_S$ to an approximate asymptotic value of $E_0 \approx 2.1$ eV. This suggests, for the sputtering condition employed, that high $T_S$ films tend toward an anneal stable state. The results are thus similar to those in a-Ge which also indicate that high substrate or annealing temperature for evaporated films yield a saturation of $E_0$ (7).

Evidence that $E_0$ is modified by structural order is shown in Fig. 4, where the ratio of x-ray diffraction
intensities, $I_1/I_2$, is compared to the optical gap. The intensity, $I_1$ is that of the low-angle diffraction peak at $k = 1.1 \text{ Å}^{-1}$, whose presence in a-As, a-P and a-As(Ge)-chalcogenides has been interpreted in terms of intermediate-range order between 10-30 Å \((8,9)\). $I_2$ is the intensity of the 'normal' diffraction peak in a-P at $k = 2.3 \text{ Å}^{-1}$. For a layer-like model suggested for the structure of a-P films, $I_1/I_2$ is a measure of the fraction of material that is locally parallel \((1,10)\). As such, this ratio will be a function of both interlayer and intralayer structural correlations. The variation of $E_0$ with increasing $I_1/I_2$ indicates that intermediate-range order modifies the electronic states and optical properties of ordered a-P films. Further evidence is also provided by the variation of the Raman spectra with $E_0$. That intermediate-range order may substantially modify the electronic wavefunctions of amorphous solids is reasonable, given recent theoretical studies \((11)\) in a-Si which suggest that the dihedral angle distribution and ring statistics may influence the optical gap. The relatively larger shift of $E_0$ in Fig. 4 for the lowest $T_s$ suggests, however, that other structural factors involving short-range order modifications may play a role with increasing disorder. This is also consistent with weaker variations in the Raman intensity for selected spectral features in the depolarized component in lower $T_s$ films \((1)\).

Further evidence for the role of intermediate-range order on the optical gap is suggested by parallel behavior observed during photostructural transformation of a-As-chalcogenide bulk glasses \((12)\). In particular, during this transformation both $E_0$ and $I_1/I_2$ decrease in a manner qualitatively analogous to that observed in a-P films with decreasing $T_s$. Though the detailed $I_1/I_2$ ratio has not been published in a-As$_2$S$_3$, the spectra suggest a somewhat similar relative variation with $E_0$ to that observed in a-P films. In addition, recent nqr measurements
(13) in a-As-chalcogenides have shown that the line shape is unchanged during photostructural modification. This implies, given the local sensitivity of nqr measurements to short-range order, that the photostructural effect must be associated with variations in order over an intermediate range. The results in a-P and the related behavior of bulk a-As-chalcogenides suggests a common origin that involves the role of intermediate-range order on the electronic states near the band edge of amorphous semiconductors. The analogy is strengthened by the observation that thin film a-P at high T_s values is an anneal stable state analogous, from a free energy point of view, to that of the bulk chalcogenide glass. Under such conditions it is most reasonable that intermediate-range order may influence the properties of noncrystalline solids.

*Supported by NSF Grant DMR 79-08390

References