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Strongly enhanced optical absorption in quench-deposited amorphous AgI films

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Amorphous AgI films prepared by quench deposition are characterized by markedly stronger optical absorption than crystalline films, by a factor more than ten in the exciton transition-energy region. They crystallize in the zinc-blende structure exhibiting well-defined crystallization temperatures dependent on the thicknesses, from 220 K (thick) to 180 K (thin). The strong absorption in the amorphous state cannot be explained by the familiar relaxation effect of the k-conserving selection rule, suggesting a fundamental change in the short-range order due to amorphization. Under the new short-range order, a considerable amount of the metal d electrons take part in low-energy optical absorption together with the I p electrons, due to p-d hybridization. [S0163-1829(98)04820-6]

I. INTRODUCTION

The compound AgI is known to undergo three phase transitions at normal pressure.[1] Up to 408 K the zinc-blende lattice (γ-AgI) is stable. In the range 408–419 K the compound crystallizes in the wurtzite lattice (β-AgI) and above 419 K it has the characteristic AgI lattice (α-AgI). In the α phase, the I^- ions occupy the bcc lattice, whereas the Ag^+ ions are more or less statistically distributed over several possible sites in the unit cell; due to such a free-ion-like character of Ag^+ ions, not only α-AgI,[2] but also AgI-based mixed systems with bcc lattice[3,4] show superionic conductivity. On the other hand, under hydrostatic pressure, AgI shows several phase changes; at room temperature, for example, from γ-AgI to the tetragonal, rhombohedral, and rocksalt modifications, depending on the magnitude of the pressure.[5]

Because of such instability against the phase transitions, the production of AgI films requires special precautions. For example, the films evaporated in vacuum onto a silica-glass substrate at 420 K, though being in the α phase at that temperature, result in γ-AgI after cooling to room temperature.[6] For evaporation at 297 K, however, one observes unstable β-AgI.[6,7]

There are several reports on electronic energy-band calculations of AgI.[5,8–12] According to Ref. 12, γ-AgI has the direct energy gap at the Γ point in the Brillouin zone, with the hybridization of Ag d states and I p states for the valence-band wave functions. This gives an account of the band-gap exciton absorption observed for the γ-AgI film.[6]

In the last ten years, the glass-forming tendency of AgI-based materials has been the subject of several works,[13–17] and it has been shown that most of the AgI-based halide glasses, achieved in a form of thin plates, are characterized by superionic conductivity due to randomly distributed Ag^+ ions.[15–17] Vaidhyanathan *et al.* have pointed out the possibility for new applications of the fast ion conductivity glasses to electrical switching devices.[18]

As for film samples, a structural study was made on noncrystalline AgI films by Rühl.[19] AgI films quench-deposited onto aluminum substrates cooled to 20 K were x-ray amorphous. The films, when warmed to 90 K and kept at that temperature, were still in the amorphous state, but they exhibited crystalline diffraction patterns when annealed at 200 K. The same effect was also observed for CuI films.

Recently we reported spectroscopic measurements of amorphous CuI films obtained by quench deposition onto silica-glass substrates cooled to 77 K.[20,21] They showed extremely enhanced optical absorption leading to an entirely different spectral profile than that of crystalline films. Such an anomalous enhancement of optical absorption due to amorphization has not been reported either on covalent semiconductors or on other metal halides as far as we know. In the present work, a similar result was observed for AgI. Specifically the extremely enhanced optical absorption of the amorphous film was confirmed by directly comparing the absorption spectra between the amorphous and the γ-phase crystalline films deposited simultaneously onto two discrete substrates put on a single sample holder, one cooled to 77 K and the other heated to 420 K, and a thorough discussion was made on the origin of the anomalous absorption in the amorphous state.

II. EXPERIMENT

Simultaneous measurements of optical absorption and reflection were performed *in situ* on AgI films quench-deposited onto silica-glass substrates at 77 K at a rate of about $20\,\mathrm{nm\,min}^{-1}$. The deposition was carried out in a vacuum of about 9×10^{-6} Pa using a tungsten basket heating element placed 8 cm in front of the substrate. The spectral measurements (resolution, 0.2 nm) were performed by a double-beam detection method, using a grating monochromator in combination with a 150-W xenon lamp as a light source.

To measure not only strong absorption of the amorphous film, but also very weak absorption after crystallization of the same film accurately, we employed the optical configuration shown in Fig. 1 (where the reference-light path in the double-beam detection method is omitted). The p-polarized monochromatic light is incident on the substrate at an incident angle of 45°. The optical density (OD) of the film was defined as

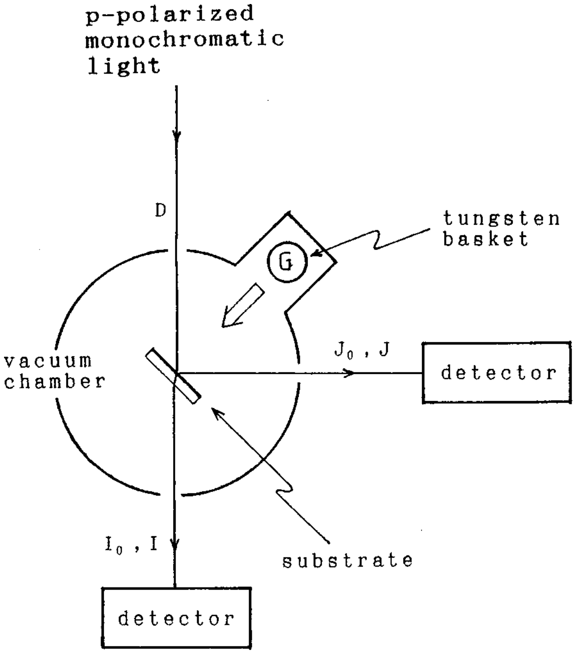

FIG. 1. The schematic view of the light path for *in situ* measurements of reflection-corrected OD spectra of a film quench deposited onto a cooled (to 77 K) substrate.

$$O_D = \log_{10}\frac{D-J}{I} - \log_{10}\frac{D-J_0}{I_0}, \tag{1}$$

where D is the intensity of the incident light, I_0 and J_0 are the intensities of transmitted and reflected light, respectively, from the substrate before the deposition of the film, and I and J are the corresponding light intensities after the film deposition. The first term in Eq. (1) corresponds to the optical density of the film-deposited substrate and the second term is the optical density of the substrate. Correction for reflectance at the film surfaces (both the film/substrate and film/vacuum interfaces) is involved in the first term. It is possible to represent Eq. (1) in terms of quantities independent of characteristics of the two individual detectors (such as sensitivity, its wavelength dependence, etc.),

$$O_D = \log_{10}\frac{1-R_0R_r}{(1-R_0)T_r}, \tag{2}$$

where $T_r = I/I_0$, $R_r = J/J_0$, and R_0 is the reflectivity of the substrate. Then the values of OD can be determined from the measurements of the intensity ratios (T_r and R_r) of the light beam irradiating the individual detectors before and after the film deposition, using the predetermined values of R_0. The OD values thus determined are expected to be very accurate, since the optical configuration is kept unchanged throughout all the measurements and since all the unbalances in intensity between the probing and reference light are canceled out.

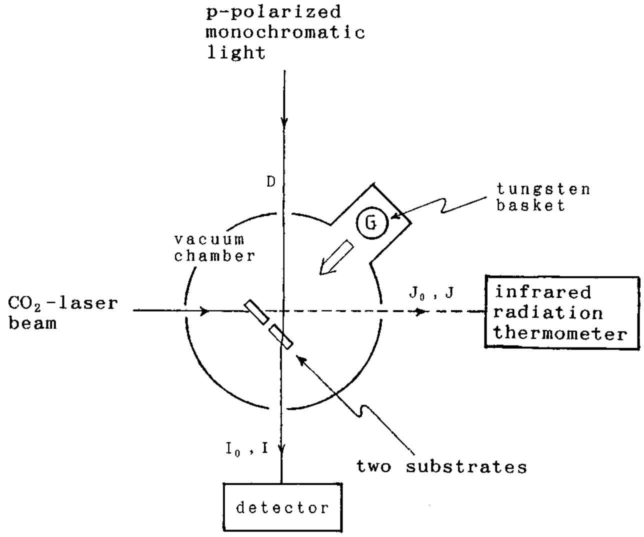

FIG. 2. The geometrical configuration for depositing amorphous and crystalline films both simultaneously onto cooled (to 77 K) and CO_2-laser heated (to 420 K) substrates, respectively; *in situ* measurements of OD spectra are available for both films by rotating the substrate holder (see text).

The substrate (silica glass with 1 mm thickness) was put on a copper sample holder with a square-light path $4\times 4\ \mathrm{mm}^2$, attached to the bottom of a copper vessel in a cryostat. The vessel was filled with liquid nitrogen, or heated with a heater to control the temperature of the substrate. This permits us to measure *in situ* OD spectra both for the amorphous and crystalline phases of the same film and the crystallization temperature as well.

As will be shown in the next section, the absorption intensity of the amorphous film is extremely large compared to that of the crystallized film. Indeed, this is so anomalous that one might suspect the film to exfoliate or reevaporate during the crystallization. To minimize such an effect, we devised the apparatus for depositing both amorphous and crystalline films simultaneously onto two discrete substrates put on a single sample holder (with two $4\times 4\ \mathrm{mm}^2$ light paths), as shown in Fig. 2. During the deposition, one of the substrates is heated to 420 K by irradiation with a CO_2-laser beam (wavelength, 11.6 μm), while the other is at 77 K (Teflon and copper sheets, both 0.5 mm in thickness and both with a $4\times 4\ \mathrm{mm}^2$ light path, are interposed between the sample holder and the respective substrates). The temperature of the heated substrate (on the Teflon sheet) is measured with a homemade infrared radiation thermometer made of an integrated thermocouple (Thermopile from Mitsubishiyuka) incorporated with a set of IR lens optics. Since the substrates are set to be rotatable about the axis that is perpendicular to the plane of incidence and that passes through the center of the vacuum chamber, it is possible to measure OD spectra of both films *in situ* [but the R_r data in Eq. (2), not measured, are taken from the corresponding data measured under the configuration shown in Fig. 1]. The equivalence in the geometrical configuration for the two substrates with respect to the tungsten basket was checked by comparing the spectra of the two films deposited simultaneously without laser heating; the difference in the OD values between the two films was within a few percent.

Finally, mention should be made of the determination of the thickness of our films. We did not measure the thickness of the amorphous films, but instead we determined that of the crystallized films using a value of optical density measured after the crystallization. Since the crystallization resulted in the γ-phase crystalline state (see next section), the film thick-

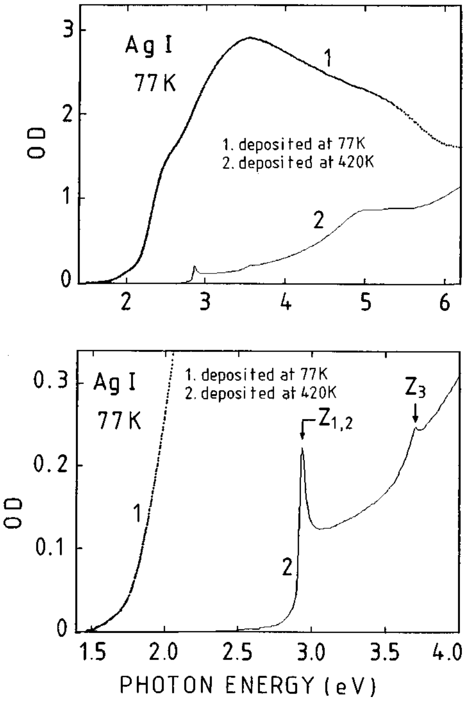

FIG. 3. The spectral comparison between two films deposited onto 77 and 420 K substrates under the configuration shown in Fig. 2. The film thickness determined in the γ-phase crystalline state is about 34 nm.

ness was given for that state. For this purpose, we measured absorption coefficient (at a particular photon energy) of the γ-phase crystalline film deposited onto a silica-glass substrate heated to 420 K. The measurement was made *in situ* on a separate vacuum-evaporation setup equipped with a quartz oscillator and a line-spectrum light source (low pressure Hg lamp with a 253.7 nm line band-pass filter). The measured absorption coefficient, 5.5×10^5 cm^{-1} at 4.887 eV at room temperature, was employed as a standard for determining the thickness of the crystallized films.

III. RESULTS

Figure 3 is the comparison of OD spectra at 77 K between two films deposited simultaneously onto discrete substrates, one cooled to 77 K (spectrum 1) and the other heated to 420 K (spectrum 2). The film thickness (determined in the γ-phase crystalline state) is about 34 nm. As seen in the lower panel (expanded view near the fundamental absorption edge) of the figure, spectrum 2 exhibits the $Z_{1,2}$ and Z_3 exciton peaks characteristic of γ-phase crystalline AgI (Ref. 6) (the absorption coefficient in the exciton transition region is comparable in magnitude to that in Ref. 6). On the other hand, spectrum 1 is characterized by extremely strong absorption over the whole measurement spectral range (upper panel) compared to spectrum 2: For example, in the exciton-transition energy region (3–4 eV), spectrum 1 has more than ten times larger optical densities than spectrum 2; at the same time an about 1 eV lower optical energy gap is exhibited for spectrum 1.

The film deposited at 77 K was subjected to the subsequent measurement of continuous change in the optical density at 3.54 eV during slow increase of temperature. The result is shown in Fig. 4. In the measurement, the as-deposited film was heated at a rate of about 1 K min^{-1} up to 300 K (curve 1) and then the film was immediately cooled to 77 K prior to measuring the second curve (curve 2). Curve 1 clearly shows a drastic decrease in the optical density at temperatures near 220 K, while curve 2 no longer exhibits such a marked change and was shown to be of a reversible nature (below 300 K) from the measurement of a third curve. We note here that the optical density at 77 K for curve 2, 0.19, was nearly equal to the corresponding OD value of spectrum 2 in Fig. 3, 0.18 at 3.54 eV (the OD spectrum at 77 K after the measurement of curve 1 was confirmed to exhibit the same outline as spectrum 2 in Fig. 3). Therefore, the drastic change in curve 1 (Fig. 4), which is very similar in sharpness to previous results on amorphous CuI films,[21] provides clear evidence of a phase transition from amorphous to crystalline states in the quench-deposited film for AgI (and also for CuI), and negates the suspicion that the film exfoliates or reevaporates during the drastic change. The transition temperature (crystallization temperature T_c), which we defined as the temperature determined by the extrapolated point P shown in the figure, is 216 K, nearly equal to that (211 K) for CuI.

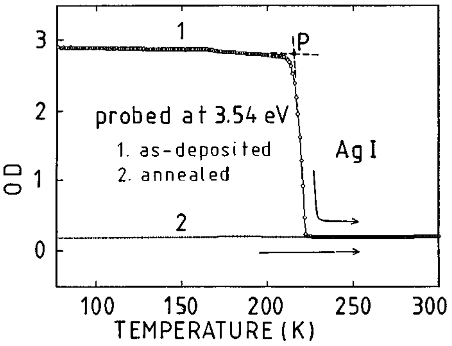

FIG. 4. The change in optical density at 3.54 eV during slow heating ($1\ \mathrm{K\,min}^{-1}$) of a film deposited onto a 77 K substrate, whose spectrum is shown in Fig. 3 as spectrum 1. The film thickness determined in the γ-phase crystalline state is about 34 nm.

We determined T_c for various film thicknesses in the same way. The results are shown in Fig. 5, where the abscissa is the optical density at 3.54 eV in the amorphous state; $O_D=1$ on the abscissa corresponds to 12 nm thickness of the crystallized (into γ-AgI) film. As seen from the figure,

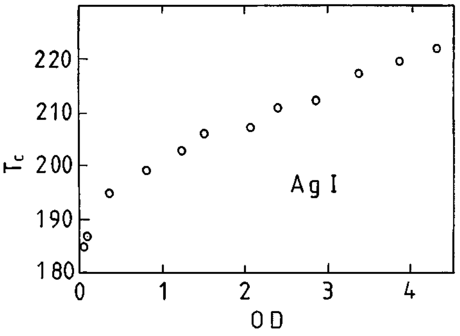

FIG. 5. The crystallization temperature T_c as a function of the amorphous-state optical density at 3.54 eV.

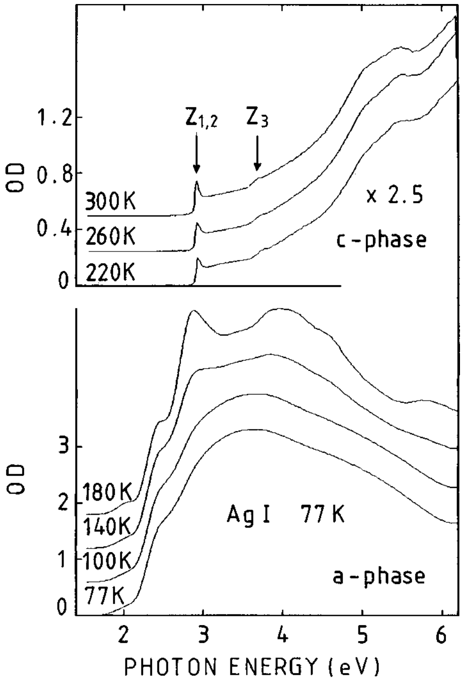

FIG. 6. The effect of annealing on the absorption spectrum of a quench-deposited film. The scale on the ordinate is given only for the lowest spectra in both panels, labeled 77 (lower panel) and 220 K (upper panel); note the magnified scale for the upper panel. The film thickness determined in the γ-phase crystalline state is about 40 nm.

T_c decreased with decreasing film thickness, more and more for $O_D<1$. Similar tendency was also observed for CuI (not shown in the figure). The lower T_c's for thinner films are attributable to surface effects: the film surfaces have the effect to lower the nucleation activation barrier and grain growth activation barrier.

Figure 6 illustrates the effect of annealing on the spectral structure of a film deposited at 77 K. The film thickness (determined in the γ-phase crystalline state) is about 40 nm. Spectral measurements were carried out at 77 K for increasing annealing temperatures as indicated. The annealing time was 10 min for each. Heating and cooling in each annealing cycle were performed at rates of 1 and 20 K min^{-1}, respectively.

As seen from the figure, the spectrum in the amorphous phase became rich in structure with increasing annealing temperature up to 180 K; the behavior is in contrast to the case of CuI, where almost no effect of annealing is observed in the amorphous phase. This reflects that the amorphous AgI film may relax to achieve better-defined short-range order than in the CuI case by thermal events before crystallization. On further annealing at 220 K, there occurred an abrupt change in the spectrum due to crystallization, giving rise to the drastic reduction in absorption intensity (note the magnified OD scale for the crystalline phase) over the whole measurement spectral range as expected from Fig. 4. The resultant spectrum showed the same outline as that of the γ-phase crystalline film deposited at 420 K (Fig. 3), exhibiting the $Z_{1,2}$ and Z_3 exciton absorptions. It is interesting to note that the amorphous film crystallizes into the γ phase (even at 220 K) without passing through the (lower-temperature) β phase. Further annealing at higher temperatures brought about little change in the spectrum.

IV. DISCUSSION

As is well known, valence and conduction bands in semiconductors retain their meaning even in the amorphous state, and the density of states (DOS) of the bands is almost unaltered by amorphization since the gross feature of electronic states is determined by the short-range order. But the lack of the long-range order in the amorphous state leads to the relaxation of the k-conserving and/or symmetry-imposed selection rule. Such a relaxation sometimes gives rise to a significant result, particularly in the case of indirect-band-gap semiconductors. For example, optical absorption in Si is strongly enhanced by amorphization in the otherwise weak-absorbing (due to indirect transitions) photon-energy region near the indirect band gap, 1–3eV.[22] It is nevertheless still important to recognize that there exists a global similarity in the spectral outline between the crystalline and amorphous states (as is indeed the case in Si) as far as the main feature of the DOS functions for the energy bands are based on the same short-range order.

In the case of AgI, where the amorphous films transform to the γ-phase crystalline films, the situation seems to be somewhat different. γ-AgI is known to have a direct band gap at the Γ point with the allowed type of optical transition matrix element between the band edges (see, e.g., Ref. 12). Therefore, the observed large redshift (blueshift), by ~ 1 eV, due to amorphization (crystallization) cannot be attributed to the relaxation (requirement) of the k-conserving selection rule, nor to the relaxation (requirement) of the symmetry-imposed selection rule at the Γ point. More important is the fact that there is no global similarity in the spectral outline between the crystalline and amorphous states. In particular, the absorption intensity is too largely enhanced by amorphization over the deep interband energy region to interpret in terms of the relaxation effect of the selection rules: no matter how completely the selection rules are relaxed, the amorphous film could not exhibit more than ten times larger optical densities than the crystallized films in the strongly absorbing, or, direct-transition, photon-energy region (3–4 eV in Fig. 3) as far as the short-range order (and thus the main feature of the DOS functions) is unaltered by amorphization. Therefore, the chemical bonding responsible for the short-range order that exists in the crystalline state is considered to have changed into a different one by amorphization.

Such anomalous change in the short-range order due to amorphous/crystalline transformation is not too surprising in view of the polytypism of AgI mentioned in Sec. I. For example, the rocksalt modification has the indirect band gap with the valence-band edge at the L point and the conduction-band edge at the Γ or X point.[11] This might account for the amorphization-induced redshift. However, the calculated DOS is not ''too largely'' different from that for γ-AgI (unfortunately, fundamental optical absorption spectrum extending into deep interband energies is not available for the rocksalt modification). Anyhow, the new short-range order in the amorphous state should be based on a new scheme of chemical bonding in which the metal d wave functions, as well as I p wave functions, contribute in such a way that a considerable amount of the d electrons with a high DOS take part in low-energy optical absorption, although the identification of the associated crystal-structure type is a future problem.

To obtain a measure of the integrated absorption intensity, we roughly estimate the effective number of electrons per AgI molecule contributing to the absorption, n_{eff}. The quantity is defined as

$$n_{\mathrm{eff}}(E)=\frac{4m}{h^2e^2N}\int_0^E E'n(E')k(E')dE', \tag{3}$$

where m is the electron mass, N is the number of AgI molecules per unit volume, E and E' are the photon energies, and n and k are the real and imaginary parts of refractive index. Since the value of N for the amorphous film is unknown, it is better to employ an alternative expression for Eq. (3),

$$n_{\mathrm{eff}}(E)=\frac{(\ln 10)mc}{he^2Nt}\int_0^E n(E')O_D(E')dE', \tag{4}$$

where t is the film thickness. Here, the product Nt remains constant throughout the amorphous and crystalline states for a given film because Nt multiplied by the film area is the net number of AgI molecules in the film; thus Nt is given by the γ-AgI value. Therefore, we can obtain a rough estimate of $n_{\mathrm{eff}}(E)$ by replacing $n(E)$ (which is unknown both for the amorphous and the crystalline states) by an ‘‘averaged’’ index n_{av}. From the OD spectra in Fig. 6 (curves labeled 77 and 300 K), n_{eff} is determined at $E=6$ eV to be 3.6 n_{av} for the amorphous state and 0.74 n_{av} for the γ-AgI state using Eq. (4). [The value of n_{av} may be of the order of 1 or 2 for both states; according to an f-sum rule, $n(E')$ in Eqs. (3) and (4) can be replaced by 1 in the limit $E\rightarrow\infty$, integral up to ∞, see Eq. (10) in Ref. 23.] Therefore, it turns out that a considerable amount of Ag $4d$ and I $5p$ electrons of total 16 electrons take part in optical absorption below 6 eV in the amorphous state (also note the decreasing optical densities in the range towards high energies in Fig. 6, lower panel), in contrast to the case of the crystalline state where the main parts of these electrons contribute to the deeper-energy optical absorption above 6 eV (note the increasing optical densities towards high energies, upper panel in Fig. 6).

The same discussion may also apply to the previous results for CuI apart from the detailed or quantitative difference.

We are ready to measure dc and ac conductivity of the amorphous film to observe, if any, superionic conductivity such as reported for AgI-based halide glasses.[13–16] The measurement may provide further information on the nature of the short-range interaction that is based on the above-mentioned p-d hybridization.

V. CONCLUSION

Amorphous AgI films prepared by quench deposition exhibited extremely enhanced optical absorption compared to crystalline films. This was confirmed by directly comparing the absorption spectra between the amorphous and the γ-phase crystalline films deposited simultaneously onto two discrete substrates put on a single sample holder, one cooled to 77 K and the other heated to 420 K. The amorphous films exhibited well-defined crystallization temperatures dependent on their thickness, from 220 (thick) to 180 K (thin), yielding the γ-phase crystalline films. The extremely enhanced optical absorption in the amorphous state cannot be explained by the familiar relaxation effect of the k-conserving and/or symmetry-imposed selection rules, suggesting that there occurs a fundamental change in the short-range order, and thus in the density of states, by amorphization. A possible explanation is p-d hybridization such that a considerable amount of the metal d electrons take part in low-energy optical absorption together with the I p electrons due to the change of the short-range order.

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