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Photoconductive and Photovoltaic Properties in Cadmium Bismuth Aluminate Glasses

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Photo-induced phenomena such as photoconductive and photovoltaic effects were investigated for the glasses in $CdO-Bi_2O_3-Al_2O_3$ system. Photoconductive effect was characterized by a slow decay of photocurrent (persistent photoconductivity). The decay rate decreased with increasing CdO content and decreasing Bi_2O_3 content. Photovoltage was very small at room temperature but increased to an obvious value on heating. The photoconductivity and photovoltage were increased with CdO content and enhanced by heat treatment in air. The valence band spectra of X-ray photoelectron spectroscopy showed that the hybridization of Cd 4d and O 2p orbitals increases with decreasing Bi_2O_3 content and increasing CdO content in the glasses. As the results of the p-d hybridization, the band structure of the glasses became indirect and the valence-band maximum tends to flat. This type of band structure inhibits the rapid recombination of electrons and holes. The persistent photoconductivity of the glasses may be attributed to deep energy level of DX centers. Deep energy levels of the glasses are able to prevent the recombination because they have a repulsive barrier for both electron emission and capture.

Keywords: Photoconductivity, Photovoltage, Persistent photoconductivity, $CdO-Bi_2O_3-Al_2O_3$ glasses, Electronic state

1. INTRODUCTION

It is well known that oxide glasses containing a large amount of CdO are photosensitive materials. They show various interesting properties such as photochromism and photoconduction [1-6]. The CdO-based glasses currently do not have any practical applications. However, they have received much attention for their photosensitive mechanism because these glasses do not contain any photosensitive crystalline particles like AgX. Investigations on the optical behavior of CdO in various host glasses may eventually helpful to fully understand the mechanism of photo-induced phenomena. Studies on various new host glasses are, therefore, of importance for the improvement of the photochromic and photoconductive properties.

The structure of $CdO-Bi_2O_3-Al_2O_3$ glass [7] was found to be contrary to Zachariasen's rules in glass formation. The oxide ions are 3 or 4 coordinated by Bi^{3+} ions, while the Bi^{3+} ions are 5 and 6 coordinated by oxide ions in the $CdO-Bi_2O_3-Al_2O_3$ glasses. Moreover, since chemical nature of Bi-O and Al-O bonds is

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distinct from an ordinal glass, change in the glass composition may affect the chemical environments around Cd ions, and it may lead to the change of the photosensitive properties. On the basis of this viewpoint, the authors have investigated the photochromic properties of CdO-Bi_2O_3-Al_2O_3 glasses [8]. The photo-induced coloration was found to strongly depend on the glass composition, and it could be effectively enhanced by oxidation treatment. The composition dependence of photochromic properties could be explained as a change in local chemical environments around Cd ions, which was suggested from Raman scattering and X-ray photoelectron spectroscopy (XPS). It was also supposed that the effect of oxidation treatment associated with production of a large amount of monovalent O^- ions [8].

It is known that ZnO and CdS crystals exhibit photoconductive and photovoltaic effects [9]. Although, oxide glasses containing CdO are photoconductive, photovoltaic activity of the oxide glasses is still not known. By adjusting the condition of photovoltaic measurement or glass composition, CdO-Bi_2O_3 glasses may show the photovoltaic effect, which would give valuable insight into the photo-induced phenomena and would increase the possibility of practical application for the CdO-based glasses.

The experiments reported in this paper are related with the studies on the photoconductive and photovoltaic effects of CdO-Bi_2O_3-Al_2O_3 glasses. The composition dependence is discussed by means of the XPS valence band spectrum.

2. EXPERIMENTAL PROCEDURE

2.1. Sample preparation

Reagent-grade Bi_2O_3, CdO and $Al(OH)_3$ were used as starting materials. A 20g batch was firstly sintered at 750 ~ 950°C for 1 hour and then melted in a high-purity alumina crucible at temperatures ranging from 1100 to 1500°C for 20 to 30 min. . The melt was poured on a stainless steel plate and the glass obtained was annealed below the glass transition temperature (Tg) for 1 hr. . The contents of Bi, Cd and Al in the glass were chemically analyzed by an inductively coupled plasma emission spectrometer. The resulting glasses were then heat-treated in air or oxygen atmosphere for 10 ~ 60 hr. below the Tg (340 ~ 600°C). The glass samples were then polished. Gold electrodes were vacuum-coated on both surfaces and a guard ring was also vacuum-coated on one surface. Thickness of the electrode was adjusted so as the electrode was electrically conductive and the surface was optically semi-transparent. The glass samples were kept in dark at 100°C for 24 hr. before the photoconductive measurements.

2.2. Electrical measurements

The electrical current through the glass was measured by a resistance meter (Yokogawa-Hewlett-Packard Ltd., HP4339A). A Xe shot arc lamp (Ushio Inc., UXL-500D-O, wavelength region at about 300 ~ 1000 nm) was used as a light source for the irradiation. The electric field of 104 V/cm was applied between the sandwich-type electrodes for the photoconductive measurement. The incident UV/VIS light was directed parallel to the electric field. Various filters (Toshiba color glass filters, the numbers in parentheses are cutoff wavelengths of the filters): V-40 (370 ~ 420 nm), V-42 (390 ~ 440 nm), V-44 (410 ~ 460 nm), B-46 (420 ~ 480 nm), Y-48 (480 ~ nm), Y-50 (500 ~ nm), Y-52 (520 ~ nm), O-55 (550 ~ nm), R-60 (600 ~ nm), R-65 (650 ~ nm) were used to measure the spectral sensitivity. The light-to-dark current ratio, I_L / I_D, was used as a parameter for the photoconduction. The I_D (dark current) and I_L (light current) were the current before and after the UV / VIS irradiation, respectively. Optical absorption spectrum was measured by using an UV / VIS spectrophotometer (Shimadzu, UV-240).

For measurements of the photovoltaic effect, the Au / glass / Au cells were equipped with a heating unit and illuminated with the light source as mentioned above. To avoid the damage due to electric field between electrodes and surfaces of glasses, we refrained from heating the samples up to 90°C. Photovoltaic voltage and current were measured by a digital multimeter (Takeda riken TR6853) and the HP4339A resistance meter, respectively. The photovoltaic voltage and current were defined as the maximum open-circuit voltage and short-circuit current respectively.

2.3. X-ray photoelectron spectroscopic measurement

The XPS spectra were measured with S-Probe ESCA (SSX-100S) spectrometer built by Fisons Instruments. A monochromatic Al-Kα source was used for excitation (hν = 1486.6eV). Clean surfaces were prepared by fracturing a rod-type specimen under an ultra high vacuum condition at a pressure of 6.7×10^{-8} ~ 1.2×10^{-7} Pa. C1s signal of adventitious hydrocarbons at a binding energy of 284.6eV was used as energy calibration.

3. RESULTS

Fig. 1 shows the time dependence of the electric current for three glasses. The glasses were subjected to the d.c. voltage in dark and then illuminated with a light. The current (I_D) gradually decreases with time when the voltage is applied in dark. The current increases instantaneously just after the light illumination and it reaches a steady state value (I_L) after about 4 min.. Interruption of the irradiation results in a steep decrease in the photocurrent, but it takes a long time for the residual photocurrent to decay to the value before irradiation (I_D). As shown in Fig. 1, three glasses have different I_L / I_D ratio and the decay time that is the period for I_L to return to the original I_D state. The I_L / I_D ratio of $5BiO_{1.5}$•43CdO•$52AlO_{1.5}$ glass is about 10^5, and the decay time is longer than 3 days in dark at room temperature. When $BiO_{1.5}$ content increases to 13 cation % with constant 43 % CdO, the ratio and the decay time decrease to 10^3 and about 50 min. respectively. It is noticed that the I_L / I_D ratio is only 10^2 and the decay time is 5 min. in the $66BiO_{1.5}$•25CdO•$9AlO_{1.5}$ glass. The decay of the residual dark conductivity could be accelerated remarkably when the samples were heated above 100°C.

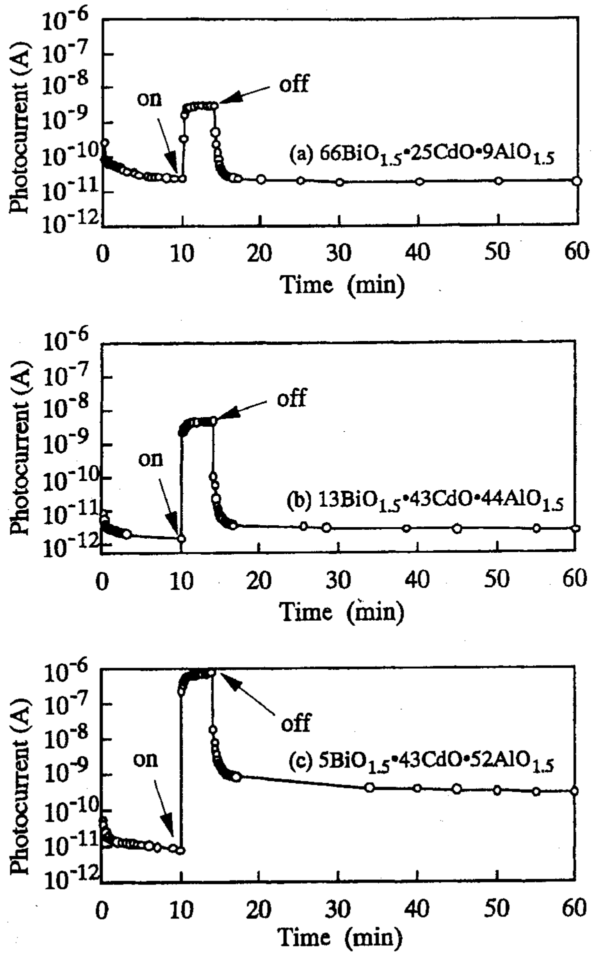

Fig. 1. Rise and decay curves of the photocurrent measured at room temperature for various glasses by irradiation of UV / VIS light.

The photocurrent and the optical absorption coefficient α of $5BiO_{1.5}$•43CdO•$52AlO_{1.5}$ glass as a function of photon energy hν are presented in Fig. 2. α and hν are expressed as : $\alpha h\nu = C(h\nu - E_g)^3$, where C is constant. The values of the optical energy gap E_g is obtained by extrapolating the expression to $(\alpha h\nu)^{1/3} = 0$. The spectral sensitivity, namely, the photocurrent as a function of photon energy [2], illustrates a sharp peak near Eg. This clearly shows that this glass is an intrinsic photoconductor where the electron is excited from the valence band to the conduction band.

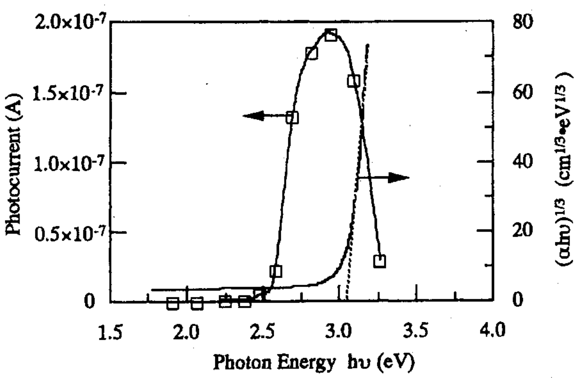

Fig. 2. Photocurrent and optical absorption coefficient as a function of photon energy for $5BiO_{1.5}$ • 43CdO • $52AlO_{1.5}$ glass heat-treated below Tg in air for 10 hours.

Fig. 3 shows the effects of composition and heat treatment on the I_L / I_D ratio for $xBiO_{1.5}$•43CdO•$(57-x)AlO_{1.5}$ (x = 5, 6, 12, 13, 25, 33) glasses. The I_L / I_D ratio increases with decreasing $BiO_{1.5}$ content. The I_L / I_D ratio is enhanced by the heat treatment in air only as $BiO_{1.5}$ content is lower than 13 cation %. When the glasses are heat-treated in oxygen atmosphere again, there is no apparent change in the I_L / I_D ratio for the glasses in contrast to photochromism. Their photochromic properties have been greatly enhanced by oxidation treatment [8]. Fig. 4 shows the I_L / I_D ratio as a function of CdO content, where $BiO_{1.5}$ content is fixed to the minimum in the glass-forming region. The I_L / I_D ratio of the as-cast glass slightly decreased with increasing CdO content, but the I_L / I_D ratio can be enhanced by the heat treatment in air. With increasing the heat treatment temperature, the glasses change in color from deep brown to weak pale yellow, and the dark current I_D was decreased. On the other hand, the as-cast glasses have also a long tail in the decay curve of photoconductivity. This is same as the result glasses heat treated in air.

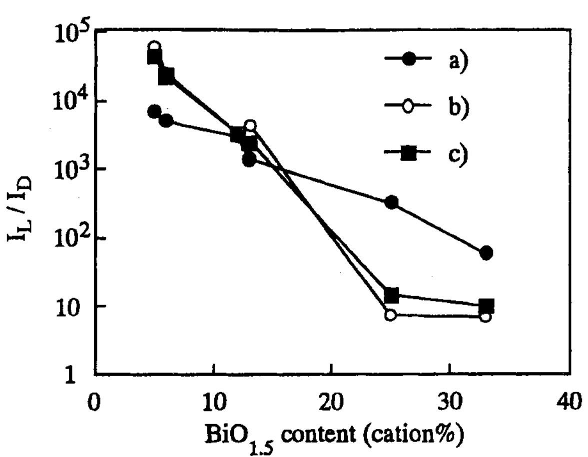

Fig. 3. The light-to-dark current ratio I_L / I_D as a function of $BiO_{1.5}$ content for $xBiO_{1.5} \cdot 43CdO \cdot (57-x)AlO_{1.5}$ glasses before and after heat treatments at various conditions. a) as-cast; b) heat treated in air below Tg for 10 hours; c) heat treated in oxygen atmosphere below Tg for

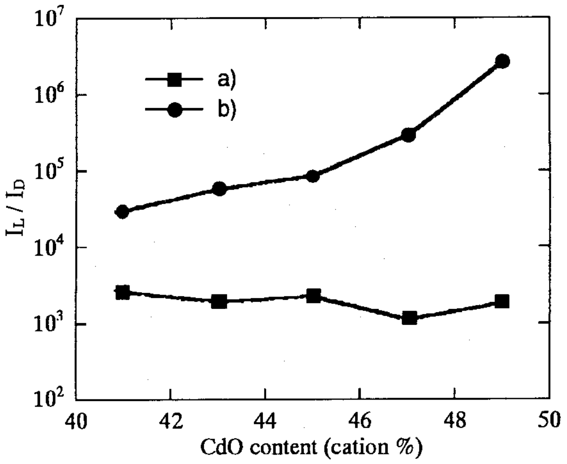

Fig. 4. The light-to-dark current ratio I_L / I_D as a function of CdO content for $5BiO_{1.5} \cdot yCdO \cdot (95-y)AlO_{1.5}$ glasses before and after heat treatments. a) as-cast; b) heat treated in air below Tg for 10 hours.

When the Au / glass / Au cells were heated and subjected to white light, the cells exhibited the

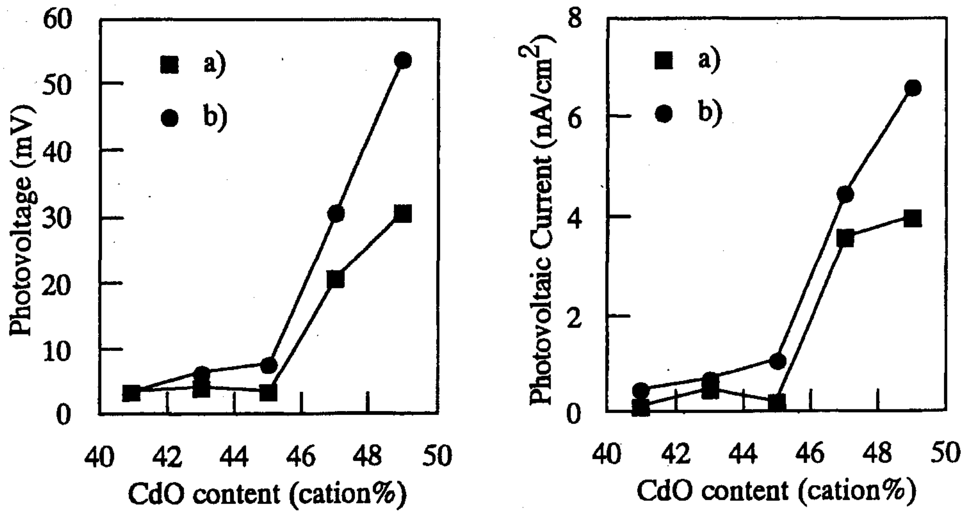

Fig. 5. Photovoltaic voltage and current at 90°C as a function of CdO content for $5BiO_{1.5} \cdot yCdO \cdot (95-y)AlO_{1.5}$ glasses before and after heat treatment. a) as-cast; b) heat treated in air below Tg for 10 hours.

photovoltaic effect. The illuminated side always became positive value. Fig. 5 shows the photovoltaic voltage and current at 90°C as a function of CdO content for $5BiO_{1.5}\bullet yCdO\bullet(95\text{-}y)AlO_{1.5}$ (y = 41, 43, 45, 47, 49) glasses before and after the heat treatment. At room temperature, only $Au/5BiO_{1.5}\bullet 49CdO\bullet 46AlO_{1.5}$ glass/Au cell exhibited a small photovoltage of 0.6 mV. As for other glasses, the photovoltage was too small to measure. As shown in Fig. 5, the photovoltage was enhanced at 90°C from 0.6 mV to 54 mV in the $5BiO_{1.5}\bullet 49CdO\bullet 46AlO_{1.5}$ glass and other glasses also could be confirmed to have the photovoltaic effect. However, without illumination at 90°C, no voltaic signal was observed for all glasses.

4. DISCUSSION

4.1. Photoconductive effect

The effects of heat treatment are explainable based on the previous studies [10-11]. The photo-induced effects, as mentioned above, are owing to light absorption due to excitation of electrons from valence band to conduction band. Therefore, if there are other light absorption sources, such as defects and impurities, the photo-induced properties should be influenced. The glasses containing Bi_2O_3 are easily colored in brown or black when they are melted above 1200°C [10-12]. In the case of low $BiO_{1.5}$ content, the darker brown may be due to a small amount of metallic Bi. When the glasses are heat-treated near Tg for longer period than 10 hr. in air, the metallic Bi are oxidized to Bi^{3+}, thus the darker brown color changes to weak pale yellow and the dark current I_D decreases by 2 ~ 3 orders of magnitude [10]. Therefore the effect of heat treatment may be resulted from the elimination of the deeper color and decrease in dark current.

The most common interpretation of such photo-induced phenomena for the CdO-based glasses is micro-phase separation [1,5]. Usually, the photo-induced phenomena such as photochromism and photoconduction are mainly related to a photo-generation yield of electrons and holes, their recombination and transport processes. However, the correlation between these processes and micro-phase separation is not understood in detail. The optical absorption in the UV / VIS-region is attributed to the excitation of electrons from valence band to conduction band. Thereby, the valence band structure measured with XPS for these glasses may be helpful to clarify the mechanism of the photo-induced phenomena. Fig. 6 shows near valence band spectra of $xBiO_{1.5}\bullet 43CdO\bullet(57\text{-}x)AlO_{1.5}$ (x = 5, 13, 33) and $66BiO_{1.5}\bullet 25CdO\bullet 9AlO_{1.5}$ glasses freshly broken in an ultra-high vacuum. The spectrum of each glass in Fig. 6 (a) is deconvoluted into three bands: (1) Bi 5d band associated with two peaks at 25-30 eV, (2) Cd 4d band with a strong and narrow peak at about 10 eV, and (3) valence band with a broad and weak peak from 8 to 2 eV. The valence band between Fermi level and 8 eV for the glasses may mainly be formed from O 2p and Bi 6s orbitals. However, the photo-induced effects of CdO-rich glasses are mainly associated with local chemical environments around Cd ions, however Cd and Bi ions cannot directly form a chemical bond. Further, the Bi 6s band is situated at top of the valence band [13], namely, the binding energy of Bi 6s band is lower than that of O 2p band. Therefore, the valence band close to Cd 4d band may primarily derive from O 2p orbital. The influence of Bi 6s band on Cd 4d band may be negligible in the case of low $BiO_{1.5}$ content.

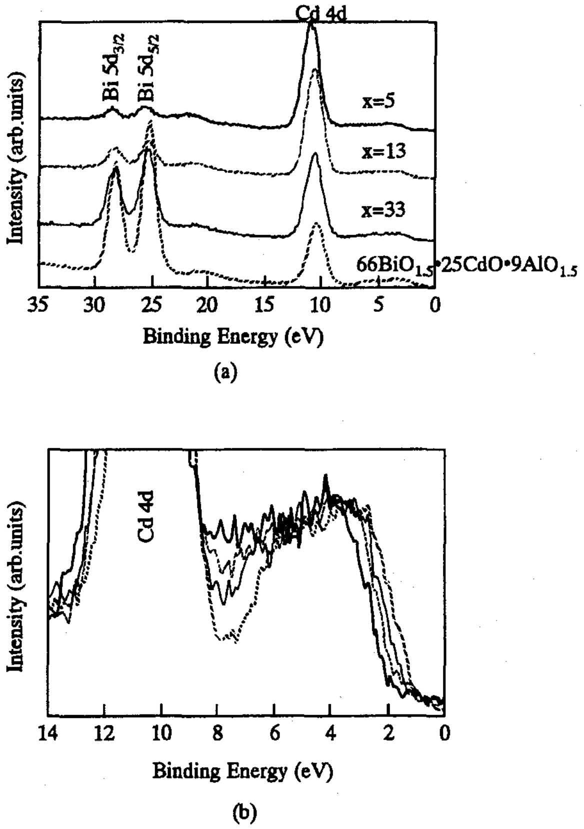

Fig. 6. (a) Valence band spectra in the region of 0 ~ 35 eV for $xBiO_{1.5}$•43CdO•(57-x)$AlO_{1.5}$ and $66BiO_{1.5}$ • 25CdO • $9AlO_{1.5}$ glasses. (b) the magnification in the region of 0 ~ 14 eV. Note changes of width and structure of the Cd 4d and 0 ~ 8 eV bands. (—— x = 5; ········ x = 13; —— x =33; ········ $66BiO_{1.5}$•25CdO•$9AlO_{1.5}$)

As shown in Fig. 6 (b), the valence band near the Fermi level shifts toward higher energy with decreasing $BiO_{1.5}$ content and increasing CdO content. This indicates that the decrease of $BiO_{1.5}$ content and the increase of CdO content lead to widen the energy gap. The measurement of optical energy gap displayed the same compositional dependence [12]. An important point to note is that the shift of the valence band is larger than that of Cd 4d near the valence band, that results in an overlap of O 2p and Cd 4d bands. As for $66BiO_{1.5}$•25CdO•$9AlO_{1.5}$ glass, the energy separation between O 2p and Cd 4d bands is very obvious. However, the separation becomes small and disappears with decreasing $BiO_{1.5}$ content in $xBiO_{1.5}$•43CdO•(57-x)$AlO_{1.5}$ glasses. This may suggest that O 2p and Cd 4d orbitals trend to overlap when $BiO_{1.5}$ content decreases and CdO content increases, or the overlap can be controlled by the glass composition. The shift of O 2p band is larger than that of Cd 4d band, implying that the overlap of O 2p and Cd 4d orbitals is mainly related to the change of electron density on oxygen atom. The glasses containing a large amount of $BiO_{1.5}$ are characterized by relatively high electron density of oxygen atom, which are as high as non-bridging oxygens in R_2O-SiO_2 (R: alkali ion) glasses, and the electron density increases with $BiO_{1.5}$ content [7, 12]. The high electron density in oxygen atoms pushes the O 2p band toward lower binding energy and lead to the increase in energy difference of O 2p and Cd 4d bands. The bond overlap between Cd 4d and O 2p orbitals, and photoconduction as well as photovoltaic effect show the same compositional dependence. It is consequently deduced that the Cd 4d electrons in CdO-rich glasses may play an important role in the photo-induced phenomena through the hybridization with O 2p electrons.

The local structure around Cd atoms in these glasses was considered to be analogous to CdO crystal [8, 13], that has a cubic structure of NaCl type with O_h space group symmetry. It is known that the effects of the p-d hybridization and repulsion cannot be ignored in energy band structure calculations of IIB-VIA semiconductors [14], such as CdO [15-16]. The overlap of Cd 4d and O 2p bands may reflect that there are the p-d hybridization and repulsion in the glasses, and this type of effect results in significant photo-induced phenomena. The octahedral symmetry in rocksalt-structure crystals does not allow hybridization of p and d orbitals at zero wave-vector because direct mixing of p and d orbitals is symmetrically forbidden in octahedral symmetry [14,17]. The hybridization is, however, allowed at non-zero wave-vectors. This hybridization produces repulsion between the p and d orbitals and forces the top of the valence band up in energy. Thus, the upper valence band for non-zero wave-vectors is repelled upward. But it does not repelled upward for zero wave-vector. As a result, the p-d hybridization and repulsion affect the maximum of the valence band so as to move away from zero wave-vector. And both the highest point of the valence band and the lowest point of the conduction band move to different wave-vector value. The band structure, therefore, tends to become indirect, and the valence-band maximum is prone to flatten [14,17]. The similar results are observed in CdO crystal, which has an indirect band gap and a very flat valence-band maximum [15-16]. As shown in Fig. 2, the optical absorption coefficient obeys the $\alpha h\nu = C(h\nu-E_g)^3$ law. This result is analogous to the variation of an indirect forbidden transition in crystalline semiconductors[18]. The very flat valence-band maximum implies a large hole effective mass [17]. Therefore the heavy holes have lower mobility, and they can be easily trapped by defects or lattice distortions. As mentioned above, the polarity of photovoltage showed always positive at the illuminated side. This reflects that these glasses obey an n-type semiconductor and only electrons contribute to electric conductivity, whereas the holes have lower mobility. Moreover, the O 1s X-ray photoelectron spectra [8] showed the presence of a large amount of monovalent O^- ions with holes in their 2p valence bands in the glasses heat-treated in air or oxygen gas. This suggests that the holes in the glasses can be trapped easily. These facts also support the hypothesis that lowering $BiO_{1.5}$ content and rising CdO content lead to produce and strengthen the hybridization of Cd 4d and O 2p bands in the glasses. As the results of the p-d hybridization and repulsion, the band structure becomes an indirect type and the valence-band maximum trends to be flattened.

The recombination of an electron and a hole is inhibited in an indirect band gap since transitions from the bottom of the conduction band to the top of the valence band are forbidden [17]. Holes in the valence band with flat maximum are easily trapped by defects because of their higher effective mass, and the recombination is also prevented. Obviously, it is favorable to have photo-induced phenomena when the band structure has the indirect band gap and the flat valence-band maximum. Such as silver bromide [19], there are also quite strong effects of the p-d hybridization and repulsion in its band structure. The indirect band gap and higher effective mass of holes seem to be important in their applications in photography. And silver bromide exhibits also photovoltaic effect [20]. Accordingly, the composition dependence of photoconductivity for CdO-Bi_2O_3-Al_2O_3 glasses may mainly be due to change in band structure with glass composition. The increase of $BiO_{1.5}$ content and the decrease of CdO content cause the effects of the p-d hybridization and repulsion in the glasses, then the band structure changes into the indirect band gap with the flat valence-band maximum. When the many pairs of electrons and holes, which are created by the incident light, are inhibited rapid recombination because of the indirect band gap, and many holes are trapped in the valence band, on the other hand many electrons will stay in the conduction band, and consequently the higher conductivity will be produced.

4.2. Photovoltaic effect

The photovoltaic effect of these glasses may be due to the Dember photovoltaic effect [21], which results from a spatially inhomogeneous carrier excitation and a large difference in the mobility-lifetime product $\mu\tau$ (τ is the carrier lifetime and μ is the drift mobility) between electrons and holes. Because of the effects of the p-d hybridization and repulsion, the holes in the valence band are heavy and easily trapped. As a result, the drift mobility μ of holes may be much smaller than that of electrons. Upon photoexcitation, the holes still stay on the illuminated side and the electrons move fast to an other side. Then, the glasses showed the photovoltaic effect. However, the photo-diffusion of electrons at room temperature may be slow and photovoltage is very low. As mentioned above, only $5BiO_{1.5} \bullet 49CdO \bullet 46AlO_{1.5}$ glass shows weak photovoltaic effect. After rising temperature up to 90°C, the diffusion of electrons is accelerated, so that the photovoltaic effect of the glass is enhanced and other glasses also exhibit an obvious photovoltaic effect. Because the photoconductive and photovoltaic properties of the glasses containing a large amount of CdO depend strongly on the effects of the p-d hybridization and repulsion, controlling the p-d hybridization via optimization of glass composition may be an effective way to improve the photo-induced phenomena.

4.3. Persistent photoconductivity

It seems from the decay curve in Fig. 1 that there are at least two recombination processes involved, namely a very rapid one that is referred to general photoconduction, and an extremely slow one that leads to the long tail in the decay curve. The excess non-equilibrium dark conductance after stopping the illumination originates from the long-lived carriers of photoexcitation. It reflects that the glasses are not in a thermal equilibrium state at room temperature. This phenomenon is often called as persistent photoconductivity [22-24]. Here, two possible interpretations are provided for the persistent photoconductivity of these glasses. The first assumes that there are micro-phase separations in the glasses. One phase in the micro-phase separations is rich in CdO that may be an n-type semiconductor. Another is an Al_2O_3 and/or Bi_2O_3-rich phase that may behave as a p-type semiconductor. The photoexcited electron-hole pairs can be separated by the p-n junction fields [22]. The electrons get preferentially trapped in the n-region and the holes in the p-region. The recombination lifetime becomes exceedingly long because the recombination is suppressed by the spatial separation and the junctions or surface barriers.

However, as for the homogeneous glasses, another explanation based on the model of microscopic barriers may be most favorable for the persistent photoconductivity. It is known that the persistent photoconductivity with a long tail in the decay curve is observed in many III-V semiconductors [25-26]. This effect is attributed to DX centers, which are deep donor levels and have a repulsive barrier for both electron emission and capture that lead to persistent photoconductivity. The DX center was considered as a complex of the donor impurity (D) and an unknown defect (X) and thus gave the name of DX center in an early stage [23-24]. There is now strong evidence, however, that DX arises from a substitutional donor by itself [25-26]. Deep levels with similar properties of DX centers have also been observed in II-VI semiconductor materials as well as ionic crystals [25]. Different models have been proposed for this deep state [25]. It was suggested that the negatively charged broken-bond model [27] was consistent with a variety of experimental results for the DX center. In our previous studies with electron spin resonance (ESR) measurement [8,10], no ESR signal was observed in these glasses. It might reflect that the defects in the glasses, such as dangling bonds [10] and color center of photochromic glasses [8], are negatively charged. The ^{27}Al-NMR and Raman spectral measurements indicated [13] that the Al^{3+} ions participate in the form of AlO_4 as a network former and there are a lot of Al-O-Cd bonds in the glasses with high $AlO_{1.5}$ and CdO content. The role of these Cd^{2+} ions is mainly a charge compensator for the AlO_4 tetrahedra. It is generally believed that the chemical bonds between the charge compensation cations and oxygen ions are weakly linked in oxide glasses. Moreover, the holes localized in O 2p will still weaken the Cd-O bonds. As mentioned above, the holes can be easily trapped in the valence bands primarily derived from O 2p because of the effects of the p-d hybridization and repulsion. This suggests that there may be some broken-bonds such as Al-O- and -Cd, in the glass structure. Based on the negatively charged broken-bond model of the DX centers [27], it is suggested that the deep levels with some "DX center-like properties" may also exist in these glasses and they may be responsible for the persistent photoconductivity. When the glasses are exposed to light, the electrons are transferred to the conduction band and the deep levels are ionized. When the light is turned off, the electrons remain in the conduction band because the deep levels have repulsive barriers to prevent the electrons in the conduction band back to the deep levels [23-24]. Therefore, decays of the persistent photoconductivity are very slowly. On the other hands, the deep levels in the glasses are more stable than those in the semiconductors, because the persistent photoconduction of the semiconductors exhibits usually at low temperature (< 77K) [25-26], while the effect of these glasses is still obvious at room temperature. This implies that the deep levels in the glasses are somewhat different from the DX center in semiconductors. To understand the defect centers more experiments are necessary such as measurements of the donor binding energy and emission and capture kinetics of electrons from the deep levels.

5. CONCLUSIONS

The significant photoconductive and photovoltaic effects were observed in the CdO-Bi_2O_3-Al_2O_3 glasses. The photoconductivity of these glasses was accompanied by a photo-induced residual conductivity, and the decay time increased with increasing CdO content and decreasing $BiO_{1.5}$ content. The photovoltage was very small at room temperature, and it could be enhanced significantly by heating the glasses. The light-to-dark current ratio, I_L/I_D and photovoltage for the glasses were positively correlated with CdO content. They could be enhanced by a heat treatment in air for a long time. The effect of the heat treatment was referred to the elimination of the deeper color of the glasses and drop of the dark current after the heat treatment.

The XPS valence band spectra of these glasses showed that Cd 4d and O 2p bands were separated both states in the case of higher $BiO_{1.5}$ content and lower CdO content, and they transformed to overlap with each other as $BiO_{1.5}$ content decreased and CdO content increased. This suggests that there is hybridization in some degree between Cd 4d and the O 2p bands in the glasses, and degree of the hybridization varies with the glass composition. An increase in the p-d hybridization and repulsion would result in the indirect band gaps and the flat valence-band maximum. The indirect band gap tends to inhibit the direct radiative recombination of electrons and holes. The flat valence-band maximum means that the holes in such band have a large effective mass, lower mobility, and they are easily trapped by defects or by the structure distortion. Thus the recombination is also inhibited. The photoconductive and photovoltaic properties as well as their composition dependence may relate to the p-d hybridization and repulsion. As for the persistent photoconductivity, two possible interpretations were proposed. One is the model of phase separations, in which the recombination of electrons and holes is suppressed because of the spatial separation and the junctions or surface barriers. Another is supposed that there are deep levels with DX center-like properties in these glasses, and the deep levels have a repulsive barrier for both electron emission and capture which leads to the persistent photoconductivity.

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