(BL3A1)

Photoinduced Effects on the Total Photoyield of Amorphous Chalcogenide Films by VUV light

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It is well-known that amorphous materials show a variety of photoinduced phenomena. Although a large number of studies have been made on photoinduced phenomena, little is unknown about the details of these mechanism. These phenomena were studied by exciting outer core electrons with the irradiation of the visible light with the energy corresponding to the optical bandgap or sub-bandgap. Little attention has been given to photoinduced effects by exciting inner core electrons with the irradiation of higher energy photon. To obtain a wide knowledge of the photoinduced effects, it is necessary to investigate the photoinduced effects on wide energy range. In the previous reports[1,2], we have reported the photoinduced effects on the optical bandgap and the photoconductivity of amorphous chalcogenide films by the irradiation of vacuum ultra-violet (VUV) light. In the present study, we performed an in-situ study of photoinduced effects by exciting inner core electrons and observed photoinduced changes on the total photoyield in amorphous chalcogenide (a-As_2S_3) films by VUV light.

Thin films of a-As_2S_3 used for the measurements of the total photoyield were prepared onto quartz substrates by conventional evaporation technique. The thickness of the films was around 6000 Å. An electrode using Al contact was fabricated first on the substrate for the measurements of the total photoyield, before depositing the amorphous films. The experiments were performed at a BL3A1 beam line of the UVSOR facility of the Institute for Molecular Science in Okazaki. VUV light that is filtered through an Al film from undulator radiation was used to measure the total photoyield. Before illumination, the samples were annealed at 443K (near the glass transition temperature) for two hours in a vacuum. To eliminate visible lights of synchrotron radiation and higher harmonics of undulator radiation, Al film was inserted between undulator and samples. The samples were fixed in sample chamber which were evacuated below 10^{-8} Torr. The photon flux of undulator radiation through Al film was estimated from the total photoelectric yield of gold mesh.

Figure 1 shows the photoinduced change on the total photoyield as a function of number of incident photon for a-As_2S_3 films. As shown in the figure, the total photoyield is slightly decreased, but it is gradually increased and it is seems to be finally saturated. The point of the saturation in the total photoyield is dependent on the energy of the excitation light. This is a new photoinduced effect caused by exciting inner core electron. It seems that the decrease and the increase in the total photoyield are related with the light induced metastable defects creation and photodarkening.

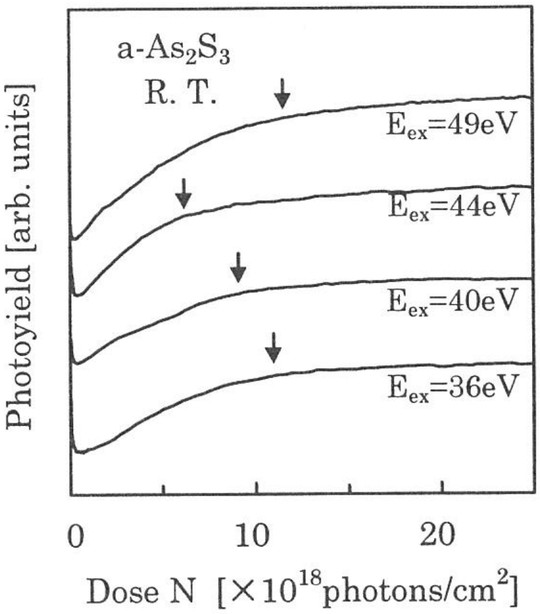

Fig.1 Photoinduced change on the total photoyield for a-As_2S_3 measured at room temperature.

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Thermal Behavior of Holes in Lead Chloride Crystal

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Excitation with x-rays or ultra-violet (uv) lights induces intrinsic self-trapping of electrons at cation sites in $PbCl_2$. The self-trapped electron (STEL) center is represented by a Pb_2^{3+} diatomic molecular ion, which consists of an electron trapped at a pair of nearest neighbor Pb^{2+} ions in the direction along the *a* axis of the $PbCl_2$ crystal [1]. On the other hand, since the valence band of $PbCl_2$ is composed of lead 6*s* and chlorine 3*p* orbitals [2,3], possibility of self-trapped holes (STH's) at lead and chlorine sites is also expected. There seems to be, however, to our knowledge, few informations on structural and electronic features, or thermal behavior of holes in $PbCl_2$ so far. They are to be a subject of extensive studies with respect to photochemical decomposition in lead halides. In the present study, thermoluminescence (TL) from the $PbCl_2$ crystal pre-irradiated by a vacuum ultra-violet (vuv) light was investigated at the temperature range from 10 K to 150 K. The TL from the x-rayed $PbCl_2$ crystal has been studied by Bettinali *et al* [4]. They measured the TL glow curve in the temperature region above 80 K and found two peaks at 126 K and 180 K. The luminescent mechanism responsible for the two peaks has not been made clear yet.

Experiments were performed at BL3A1 of UVSOR. Quasi-monochromatic light from an undulator was used as an excitation light. The $PbCl_2$ specimens were mounted on the copper holder of a variable temperature cryostat of He-flow type. TL glow curves were observed at a constant heating rate of 0.1 K/sec. The TL intensity was detected by a photomultiplier without passing it through a monochromator. TL spectra at glow peaks were measured by using a monochromator (Spex 270M) equipped with a CCD camera (Princeton LN/CCD-1152B), and were corrected for the dispersion of the monochromator and for the spectral response of the detecting system.

Figure 1 shows a glow curve of the TL from the $PbCl_2$ crystal pre-irradiated by a vuv light at 36 eV. The dotted curve in Fig. 1 is calculated one, the detail of which will be described later. The TL intensity is normalized to unity at the maximum. The TL glow curve presents newly two peaks at 51 K and 71 K, besides the peak at 126 K, but does not exhibit the peak at 180 K. From electron spin resonance (ESR) experiments by Nistor *et al.*, the STEL centers are known to be stable below 130 K. Such thermal stability of the STEL centers

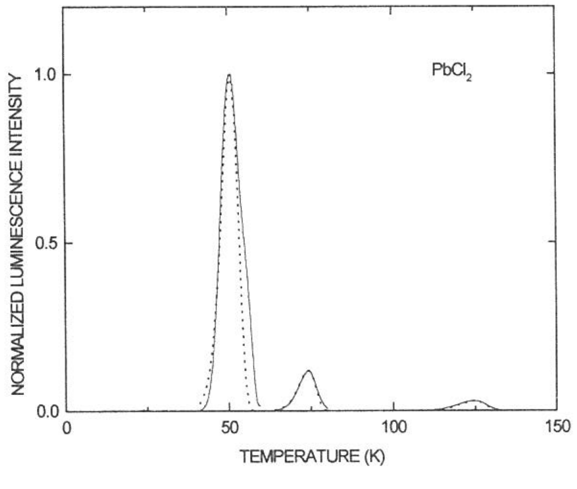

Fig. 1. Themoluminescence glow curve of $PbCl_2$.

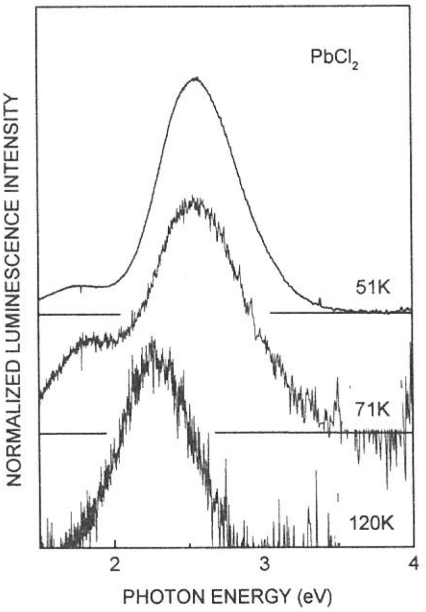

Fig. 2. Thermoluminescence spectra observed at 51 K, 71K, and 120 K

Table 1. Frequency factor ν_0 and activation energy E for each glow peak.

Peak (K)	51	71	120
ν_0 (s^{-1})	1.66×10^{9}	1.1×10^{11}	6.3×10^{11}
E (meV)	105	190	330

suggests that the two peaks at 51 K and 71 K originate from migration of holes thermally released from trapping centers. This is consistent with photoconduction studies [5] that revealed photoholes to be more movable carriers than photoelectrons in $PbCl_2$. On the other hand, the peak at 126 K would be reasonably connected to thermal decay of the STEL centers.

If de-excitation processes of electrons or holes captured by recombination centers are negligible, it is known that the TL intensity is given by

$$I(T) = n_0 \nu_0 \exp\left(-\frac{E}{\kappa T}\right) \exp\left\{-\int_{T_0}^{T} \frac{\nu_0}{\beta} \exp\left(-\frac{E}{\kappa T}\right) dT\right\}$$

where n_0 is the number of recombination centers at the temperature T_0 at which thermal stimulation is started, and β the heating rate; moreover, E and ν_0 are the activation energy and the frequency factor, respectively, for thermal migration of holes or electrons. The dotted curve in Fig. 1 is obtained by substituting the values in Table 1 for the parameters in the formula. It reproduces the TL glow curve observed, except the high-energy side of the peak at 51 K. Such deviation from the experimental data evidences the presence of a hole trapping center with slightly different structures.

The TL spectra observed at the three peaks are shown in Fig. 2. The intensity of the TL spectra is normalized to unity at the maximum of each spectrum. Two bands appear at 2.60 eV and 1.90 eV in the TL spectra at 51 K and 71 K, in which the 2.60 eV band is dominant. It was confirmed that glow curves for the two bands have peaks at 51 K and 71 K similarly. The 2.60 eV band, which is called as BG band, has been attributed to radiative recombination of a hole with an electron trapped at the STEL center [6]. This band is regarded as a intrinsic luminescence band in $PbCl_2$. The 1.90 eV band depends sensitively on sample conditions; therefore, it may be assigned to an extrinsic origin. On the other hand, another band is predominantly observed at 2.31 eV in the TL spectrum at 120 K. The origin of the 2.31 eV band is not clear at present.

Appearance of the BG band in the TL spectra at 51 K and 71 K suggests that, at least, two kinds of intrinsic hole trapping centers, that is, STH centers are created with the STEL centers. Furthermore, as far as electronic structures of the valence band of $PbCl_2$ are considered, it seems natural to expect self-trapping of holes at lead and chlorine sites in this material. Judging from these presumptive evidences, molecular ions of Cl_2^- and Pb^{3+} type are supposed to be plausible candidates for the STH centers in $PbCl_2$. The $PbCl_2$ crystal has several pairs of adjacent chlorine ions with slightly different separation and orientation, so slightly different Cl_2^- centers should be formed in $PbCl_2$. Thermal decay of the Cl_2^- centers will result in a TL glow peak which does not conform to the formula above. Actually in Fig.1, such a TL glow peak was observed at 51 K. It is, therefore, reasonable to connect thermal decay of the Cl_2^- centers to the TL glow peak at 51 K. On the other hand, the TL glow peak at 71 K probably arises from thermal decay of the Pb^{3+} centers. It is expected that, similarly to the case of alkali chlorides containing Pb^{2+} ions, the Pb^{3+} centers are formed when the Cl_2^- centers decay thermally.

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(BL3A-1)

The Initial Stage of Excitation Process by Undulator Radiation Light Using Scanning Tunneling Microscope

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In recent years, photo-enhanced chemical vapor deposition method (photo-CVD) using vacuum-ultra-violet-light (VUV-light) attracts much attention as a process technology in the following generation. However, since VUV-light in the photo-CVD process has a high photon energy, some influences to the substrate should be taken account. In order to obtain high quality functional thin films by using VUV-light excited CVD, it is important to know the initial stage on the film growth. Further investigations on the photon energy dependence are required. Scanning Tunneling Microscopy (STM) is a direct instrument working in real space on an atomic scale, and can give much information of surface reaction.

We have already clarified that the two kinds of images are observed on the sample irradiated with the Undulator Radiation (UR) : one is a dark spot and the other is a bright spot located at the center of dark circular image. The number of the patterns increased with increasing the UR light irradiation dose.

In the present work, we have investigated an effect of UR irradiation on substrate surface in vacuum with an in-situ UHV-STM.

In this experiment, we used MoS_2 as a substrate, because a clean surface can easily be obtained by the cleavage and the surface is not oxidized in air at room temperature. The UR irradiation was performed inside a reaction chamber with a base pressure below 3.0×10^{-8}torr. The undulator gap of 60mm corresponding to the 1st order photon energy of 36eV was used. Total dose was in the range of $5.0\times10^{18}\sim1.0\times10^{20}$photons/cm^2.

The surface structure was investigated on the UR light-induced defects by STM with constant height mode. The image was measured with the tip bias range of ±150mV.

Figure 1 shows the STM image of MoS_2 clean surface on the 500Å×500Å scale with the sample bias voltage of -150mV and the tunneling current of 1nA.

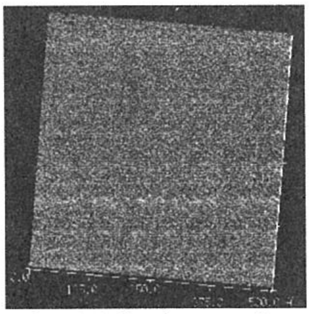
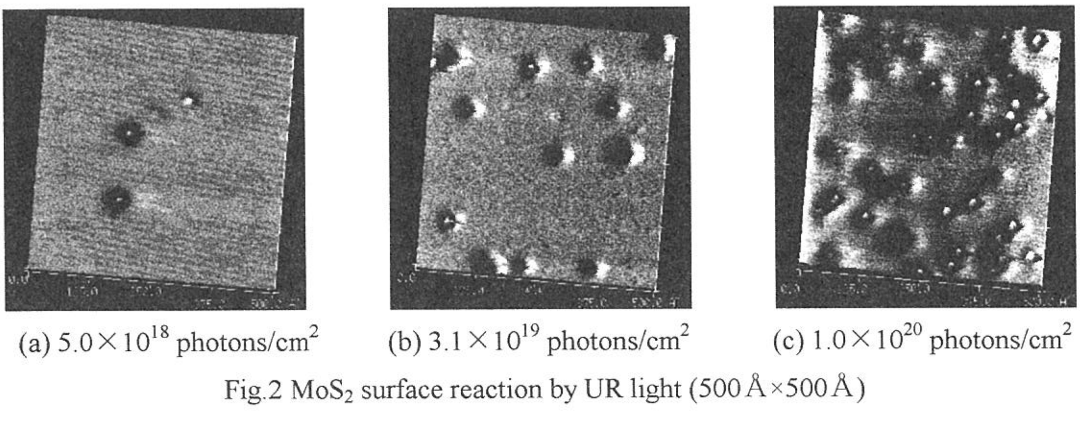


Fig.1 MoS_2 clean surface (500Å×500Å)

Figure 2(a), (b), and (c) show the STM images of MoS_2 surface irradiated by UR light for 5.0×10^{18}, 3.1×10^{19}, and 1.0×10^{20}photons/cm^2 in vacuum, respectively. These images were observed on the 500Å×500Å scale, and the tip bias was +150mV. From these images, the

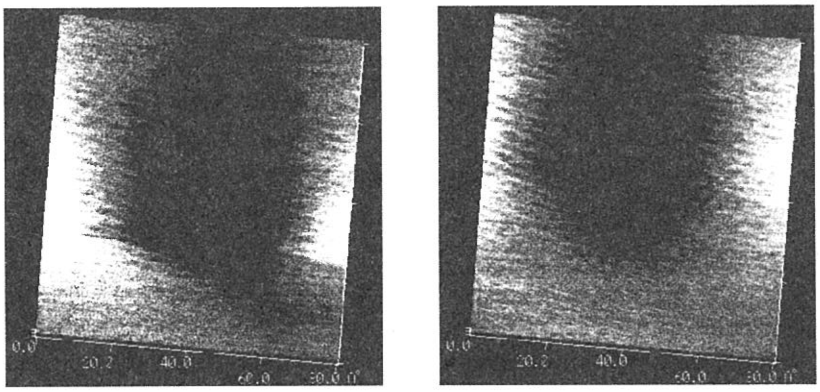


(a) 5.0×10^{18} photons/cm^2 (b) 3.1×10^{19} photons/cm^2 (c) 1.0×10^{20} photons/cm^2

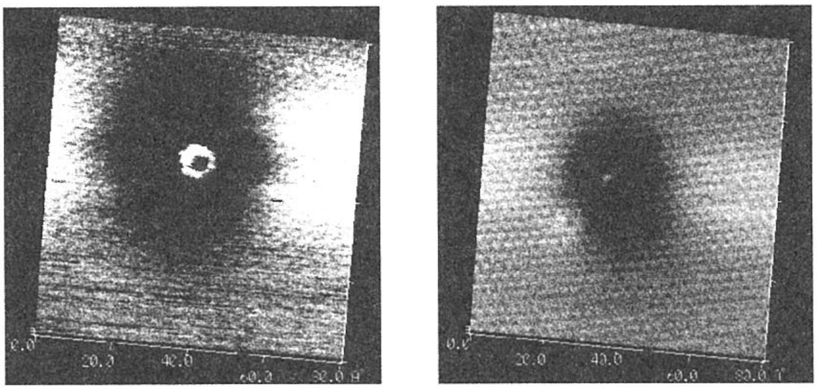
Fig.2 MoS_2 surface reaction by UR light (500Å×500Å) depression region and the ring structure were found at the initial stages of irradiation. The number of the two kinds of patterns increased with increasing the irradiated dose.

The tip bias voltage dependence of two kinds of images is shown in a Fig. 3. The sample bias voltage in Fig. 3(a-1), and 3(b-1) was 150mV, and in Fig. 3(a-2), and 3(b-2) was -150mV. These images were observed on the 80Å×80Å scale. From Fig. 3(a-1) and 3(a-2), the dark circular region did not show voltage dependence. Therefore, the dark regions in the outside and at the center of VUV photon-induced defects are considered to ablated on the surface. From Fig. 3(b-1), and 3(b-2), the bright ring pattern in the dark region was observed. The bright ring pattern in the dark region are due to the positive charge localized at the center, so it is considered that some dark regions have some electrons trapped at the center of dark region.

In summary, effects of UR light irradiation on the MoS_2 surface have been investigated using STM. With the UR irradiation, the MoS_2 surface is modified, showing the initial stages of VUV photon-induced change on the irradiated surface on the atomic scale.



(a-1) tip bias voltage : 150mV (a-2) tip bias voltage : -150mV



(b-1) tip bias voltage : 150mV (b-2) tip bias voltage : -150mV

Fig.3 STM images of the MoS_2 irradiated by UR light (80Å×80Å)