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HTML ABSTRACT + LINKS

Proton-beam-induced defect levels in $CuInSe_2$ thin-film absorbers: An investigation on nonradiative electron transitions

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Electron nonradiative relaxation through the proton-irradiation-induced defects in $CuInSe_2$ solar cell material were investigated by using a piezoelectric photothermal spectroscopy (PPTS). Among the observed three peaks at 1.01, 0.93, and 0.84 eV, it was concluded that the peak at 0.84 eV was due to the proton-irradiation-induced defect. This is because this peak appeared after irradiation with the proton energy of 0.38 MeV and the fluence of 1×10^{14} cm^{-2}. The peaks at 1.01 and 0.93 eV were attributed to free band-edge exciton and intrinsic defect level, respectively. The intensities for the latter two peaks were not affected by the irradiation. Since the irradiation defect was clearly observed at room temperature, we concluded that the PPTS technique was a very sensitive tool to study the defect level in the irradiated semiconductor thin-film solar cell structures. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1784518]

Cu(In,Ga)Se_2 (CIGS) is a promising candidate for absorber layers of future thin-film space solar cells. CIGS solar cells are known to exhibit excellent radiation tolerance,[1] while they show the highest conversion efficiency among any thin-film polycrystalline solar cell.[2] Radiation damage studies for CIGS thin-film solar cells have shown that the electrical properties, degraded by high-energy proton irradiation, gradually recover when irradiated cells are kept at room temperature.[1] However, the mechanism both for the degradation and the recovery were not clear at present. Since there are a number of vacancies and defects in this material, defect dynamics should be simultaneously taken into account for further discussion. Although some authors report on the effect of irradiation on the electrical properties of one of the end materials for the CIGS system, $CuInSe_2$ (CIS) thin films,[3] no optical studies have not been carried out yet. In the case for electron transition through the radiation-induced defects, nonradiative transition plays an important role due to the strong electron lattice interaction. Therefore, we need a complementary experimental methodology to the convenient photoluminescence (PL) to investigate such nonradiative transition. The PL technique gives us knowledge only for the radiative electron transition.

Optical absorption measurement is another conventional way to detect the defect level through the absorption coefficient. However, this technique is not adequate to observe accurate values for the low concentration of the defects, especially for the thin-film samples. The intensity of the absorbed light was usually too small to observe well-defined absorption spectra. Recently, we have developed a methodology named piezoelectric photothermal spectroscopy (PPTS) instead of a conventional microphone photoacoustic measurement.[4] For the semiconductor technology of solar cell and optoelectronic device technologies, the nonradiative centers dominate a device degradation mechanism. However we had no effective method to obtain information concerning nonradiative electron transitions until now. The proposed PPTS technique becomes, then, a useful methodology for this field. We have succeeded in studying electron deexcitation processes in the thin epitaxial layers of GaAs,[5] GaAlAs,[6] CIS,[7] and GaInNAs.[8] Quite strong signal peaks in the PPT spectra were observed, and intensive discussions for the defects and impurities were carried out. We, then applied this technique to investigate the effect of the proton irradiation on the optical properties of CIS thin films. The obtained knowledge for the CIS films might pursue an argument to the irradiation effect on the CIGS solar cells.

Epitaxial CIS films were grown on a semi-insulating single-crystal [001] GaAs substrate using a molecular beam epitaxy (MBE) system. Metallic source materials of Cu(7*N*), In(7*N*), and Se(6*N*) were evaporated simultaneously from separate Knudsen cells. The growth temperature of the CIS films was 450°C, the thickness was 1.0 μm, and the Cu/In ratio was 1.0. The secondary Cu-rich phases (such as $Cu_{2-x}Se$) at the film surface was removed by potassium cyanide (KCN) treatment to obtain stoichiometric CIS films.[9] Proton irradiation was performed on the CIS films using an ion implanter, which consists of a tandem accelerator and an azimuthally varying field (AVF) cyclotron accelerator, at the Japan Atomic Energy Research Institute, Takasaki. The en-

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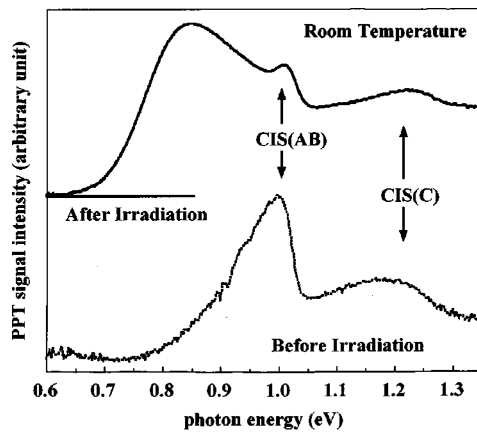

FIG. 1. PPT spectra of stoichiometric $CuInSe_2/GaAs$ samples at room temperature before and after proton irradiation.

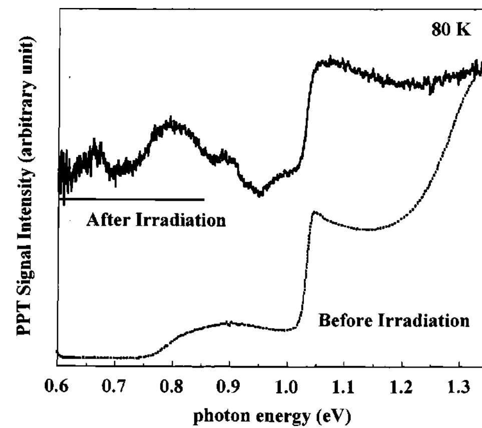

FIG. 3. PPT spectra of stoichiometric $CuInSe_2/GaAs$ samples at 80 K before and after proton irradiation.

ergy of the irradiated protons was 0.38 MeV and the fluence was 1×10^{14} cm^{-2}. The energy of the protons was chosen to provide a penetration depth of about 2 μm, in order to selectively influence the CIS film. The effect of irradiation to the GaAs substrate on the PPT signal should be negligible, as the thickness of the substrate is sufficiently large.

Figure 1 shows the changes of the PPT spectra by proton irradiation, measured at room temperature. The arrows in the figure denote the direct free-exciton transitions around 1.02 and 1.23 eV, the so-called *AB* and *C* bands of CIS, respectively. These values agree well with the reported values.[7] These peak energies were not changed by the proton irradiation. In the lower energy region below the *AB* band-to-band transition, a small hump centered at 0.93 eV was observed before the irradiation. The proton irradiation resulted in the change of the spectra below 1 eV. After the irradiation, a broad and strong peak appeared around 0.9 eV. A curve fitting for the spectra below the band-gap energy was carried out by decomposing into Gaussian functions (Fig. 2). Three distinct peaks at 0.84, 0.93, and 1.01 eV were observed. Here we refer to the peaks at 0.84 and 0.93 eV as the irradiation-induced defect (IRD) and intrinsic defect (ID) peak, respectively. The peak at 1.01 eV corresponds to the free-exciton (FE) emission. At higher energies than the FE peak, signal increases with photon energy. We have previously reported that this increment is due to the band-to-band

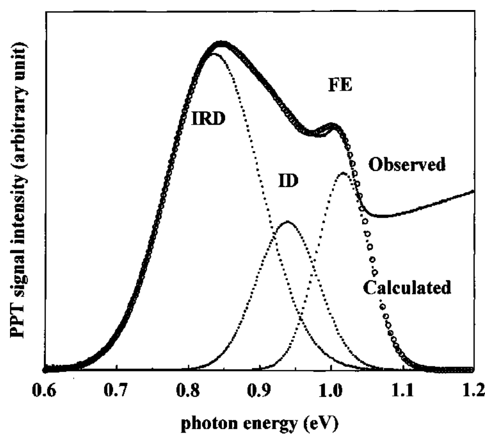

FIG. 2. Decomposition of the peak below the band gap of stoichiometric $CuInSe_2/GaAs$ samples. Solid and dotted lines indicate experimental and Gaussian fitting data, respectively. Open circles were obtained by adding all Gaussian fitting data.

transition which occurs around 1.03 eV.[10] The shape of the spectrum in this region can be described by the equation $(h\nu-E_g)^{1/2}$ of the direct allowed interband transition. The spectrum above 1 eV is also in correspondence with the optical absorption spectra reported by Chichibu *et al.*[10] However, since we are interested in the band-gap region, we will focus on the spectrum below 1.05 eV in this paper.

Before irradiation, two peaks were revealed by Gaussian fitting in the PPT spectrum. One at 1.01 eV is due to the FE peak, as discussed before, and another peak at 0.93 eV has the same peak energy to the ID peak observed after irradiation. Therefore, we consider that this ID peak is an intrinsic peak. On the other hand, the proton irradiation resulted in the appearance of the IRD peak at 0.84 eV. Preliminary photoluminescence measurements were also carried out at 1.4 K. However, no distinctive difference of the PL peaks for the samples before and after irradiation could be observed.

Compared with the conventional optical absorption spectra, the observed PPT spectra had two major advantages. First, defect levels below the band- gap were clearly observed, even at room temperature. Since the absorption intensity by such defect levels of low concentration is usually quite smaller than that of the interband transition, this high sensitivity makes the PPT method suitable for investigating the dynamics of nonradiative recombinations. Second, the FE peak was also clearly resolved at room temperature. Since the exciton binding energy is around 0.01 eV,[10] the FE peak cannot be resolved in the absorption spectra,[10] being too close to, and completely merged with, the band-to-band transition peak. In contrast, the drastic increase of the FE peak in the PPT spectrum compared with the absorption spectra indicates that the nonradiative transition probability for the dissolved exciton becomes large with increasing the temperature. If we consider that the carriers to generate the nonradiative transition should overcome the potential barriers as suggested by Pankove,[11] the probability increases with increasing the temperature. Furthermore, if the band-to-defect level transition includes the lattice distortion, a configuration coordinate diagram is also used for the transition process.[11] In this case, the nonradiative transition probability increases with increasing the temperature. This results in the decrease of the signal-to-noise ratio in the spectra at low temperature, as shown in Fig. 3.

The low-temperature PPT spectra for the stoichiometric samples before and after the proton irradiation are shown in

Fig. 3. The temperature of the sample was cooled down to 80 K in the liquid nitrogen cryostat. The free-exciton peak shifts to the higher energy side and appeared at 1.04 eV. At the same time, exciton intensity decreased compared with the PPT signal above the band-gap energy. The observed spectral shape above the free-exciton energy becomes similar to that obtained from the optical absorption measurements. Although no effect of irradiation on the spectra above the free-exciton peak was observed, the hump around 0.9 eV became clear at low temperature. The appearance of this broad peak might be due to the fact that the width of the FE peak decreased. The lifetime of the free exciton increases at lower temperatures.

After irradiation, three peaks at 0.65, 0.8, and 0.9 eV were observed at 80 K (Fig. 3). If the IRD peak observed at room temperature at 0.84 eV still remains below 80 K, the peak energy should shift 0.035 eV higher[7] and appear around 0.88 eV. Therefore, we consider that the observed peak at 0.90 eV is the IRD peak, which is induced by the proton irradiation. Since the quantum efficiency for the radiative transition increases at low temperature, the intensity of the PPT signal might decrease. However, the appearance of the peaks at 0.65 and 0.80 eV are hard to explain. If the above discussion for the 0.90 eV peak is applicable, large signal peaks should be observed in the room temperature PPT spectra below 0.8 eV. This is not the case in the present results. No relation with the observed peaks at 0.7 and 0.8 eV at 1.4 K in the preliminary observed PL spectrum could be concluded yet.

In conclusion, proton irradiation damage for $CuInSe_2$ (CIS) solar cell materials was investigated by the PPTS technique. Three major peaks below the band-gap energy of CIS was observed by PPTS measured at room temperature. One is due to the free exciton attributed to the so-called CIS *AB* band. No effect of the proton irradiation for the free-exciton peak was observed. The peak at 0.93 eV observed in the two samples both before and after irradiation may be due to the intrinsic defect. The most prominent peak at 0.84 eV is found to be due to the proton irradiation damages. The evident changes in the measured spectra have suggested that the PPTS technique is a powerful methodology to study the defect levels in the irradiated semiconductor thin films. Low-temperature measurements were also carried out. The PPT signal intensity of the defect levels decreased with lower temperature. This may be interpreted by considering that the electrons that undergo a nonradiative transition should overcome certain potential barriers that are usually used in the configuration coordinate diagram for interpreting the electron transition with strong electron lattice interaction.

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