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Electrically Induced Optical Absorption in Al-$CuAlS_2$-Au Diode

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Electrically induced change in absorption spectra was observed for the first time in the $CuAlS_2$-Al junction with a Schottky-type contact at 20 K in the wavelength region 600–900 nm. The observed change of absorption is considered to be due to the motion of the Fermi level on applying voltage across the level formed by some charged state at the metal-semiconductor interface.

KEYWORDS: chalcopyrite-type semiconductor, $CuAlS_2$, Schottky diode, electrically induced change of absorption, Fermi level motion

1. Introduction

In recent years, ternary compounds of the type $A^1B^3C^6_2$, crystallizing in the tetragonal chalcopyrite structure, have been attracting much interest due to their promising luminescent and nonlinear optical properties.[1]

For the technical application of $CuAlS_2$, it is necessary to understand the nature of the residual impurities incorporated in this compound, including transition atom (TA) impurities, which are known to have great influences on the optical properties of ternaries and to play a significant role in the process of electrical charge compensation. We have been studying the optical characteristics of $CuAlS_2$, especially, the optical role of TA in $CuAlS_2$.[2] We have found that TA impurities such as Fe and Cr have their own demarcation levels delineating between valence states Fe^{2+}/Fe^{3+} and Cr^{+}/Cr^{2+} in the band gap. The valence states of Fe and Cr ions and their relative concentrations in each valence state have been found to be controlled by the position of the Fermi level in the band gap of the host crystal in relation to the demarcation levels, this position being dependent on stoichiometry.[3]

Since $CuAlS_2$ has a relatively wide band gap (3.55 eV), the material should be transparent throughout the visible region. However most single crystals grown by the chemical transport technique are green or blue. It is postulated that the coloration is caused by absorption bands in the red-to-green wavelength region introduced by residual TA impurities, such as Fe^{3+}, Cr^{2+} and Ni^{3+}. We have previously shown that thermal annealing results in changes in color (absorption spectra) in $CuAlS_2$.[3] This finding was explained by Fermi level motion across the demarcation levels upon annealing, which in turn causes a change of valence, such as $Fe^{2+} \leftrightarrow Fe^{3+}$ and $Cr^{+} \leftrightarrow Cr^{2+}$. By these processes, TA ions lose or gain electrons, so that relative concentrations of ions change. Changes in color of a $CuAlS_2$ single crystal upon annealing are considered to be due to this mechanism.

Base on the results of these experiments, we conclude that the color of the chalcopyrite crystal can be artificially controlled through not only thermal treatments but also optical or electronic perturbation. We have already succeeded in realizing an optically induced change of absorption in $CuAlS_2$:Co^{2+} by irradiation of light from an Ar^+ laser, which will be reported in a later publication. subsequently, we proceeded to the next step, i.e., electrical control of optical absorption. For this purpose, studies of the metal-semiconductor (MS) contact are important. However, only a few reports have been published on the formation of MS junctions in wide-gap chalcopyrite-type semiconductors. Kobayashi et al. reported on an MS diode of Al-$CuGaS_2$ as a DC green electroluminescence (EL) device.[4] Tanaka *et al.* reported on an Al-$CuAlS_2$:Mn contact as a DC red EL device.[5] These works were only for luminescent devices and no MS diodes aimed at electrical control of absorption have been investigated.

Systematic studies on MS junction properties in $CuAlS_2$ have not been conducted. Fundamental information, such as regarding on work functions, surface treatments, and junction formation, is lacking. We therefore systematically investigated MS junctions for $CuAlS_2$ single crystals, changing the metals (Al, Au, Yb, Ag, In), etchants (HF, HNO_3, HCl, H_2SO_4, and H_2SO_4+$K_2Cr_2O_7$) and time duration for etching. Among all the combinations, only the Al-$CuAlS_2$ contact with 30 s HF treatment of $CuAlS_2$ resulted in Schottky-like current-voltage(I-V) characteristics. We measured the optical absorption spectra for this diode and found that optical absorption of $CuAlS_2$ can be changed artificially by applying on electrical field.

2. Experimental

2.1 *Crystal growth*

Single crystals of the $CuAlS_2$ compound were grown by the temperature-variation chemical vapor transport (CVT) technique in a closed system using iodine as a transport agent. The starting material used for CVT was stoichiometric elements or the powder of the polycrystalline $CuAlS_2$ compound prepared by the direct melting of constituent elements in a p-BN crucible held in a sealed quartz ampoule.[6]

The resulting $CuAlS_2$ single crystals were typically bulk ones with dimensions of about $1\times3\times5$ mm^3.

2.2 *Thermal treatments*

As-grown crystals are usually highly compensated, and show very high resistivity of one MΩ cm order. In order to reduce the resistivity, annealing of crystals in vacuum or sulfur atmosphere was performed. The sample was put into a silica ampoule and sealed in a vacuum of 1×10^{-6} Torr. For sulfur (S) annealing, the temperature was maintained at 800°C for 24 h, while for vacuum annealing, the temperature was maintained at 800°C for a few weeks. After thermal annealing in sulfur atmosphere, the $CuAlS_2$ crystal was rinsed in boiling CS_2 solution to remove the sulfur adhered on the surface.

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2.3 Schottky contact formation

Planar-type MS diodes were prepared. Two metal contacts were alternately evaporated on the surface of the single crystals with a spacing of about 1 mm. The contact metals investigated were Au, Al, In, Yb, and Ag.

Prior to evaporation, the crystals were mirror-polished and etched in different chemical solutions for different time durations to remove the damaged surface layers or surface oxides formed on the crystals, and then rinsed in deionized water. We used HF, HNO_3, HCl, H_2SO_4, and $H_2SO_4+K_2Cr_2O_7$ solutions for the chemical treatments. The etching times of 30 s, 1 min, and 5 min (longer than 10 min and 20 min at H_2SO_4) were used.

2.4 Measurements of electrically induced absorption

Thin wire contacts were soldered to metal electrodes using an In solder, in order to apply voltage to the diode placed in a cryostat. Absorption spectra were measured at 20 K, using a tungsten lamp as a light source. White light from the lamp was focused on either of the two contact areas in the planar MS diode and the transmitted light was detected by a CCD-type spectrograph (Santa-Barbara Inst. Group ST-6). Data acquisition was performed on a personal computer. The spectrograph system can immediately display optical absorption spectra in the spectral range between 500 and 900 nm for a shutter-opening period of two seconds. Background subtraction and blank measurement for absorbance also were performed. Absorption spectra with and without the application of electrical field to the diode were measured.

3. Results and Discussion

3.1 Thermal treatments

As-grown $CuAlS_2$ single crystals show high resistivity of over 20 MΩ cm at the surface region. Resistivity was reduced after polishing and etching. The resistivity of the sample with metal contacts was about 10^3–10^4 Ω cm independent of the metals used. As-grown $CuAlS_2$ single crystal shows a p-type conductivity with the Fermi level located in the midgap region. The thermal treatment in sulfur atmosphere decreases the concentration of sulfur vacancies V_S and increases the concentration of cation vacancies V_{Cu} and V_{Al}, which in turn increases the conductivity of p-type samples. As-grown samples are usually pale green or pale blue; S annealing deepens the color. As the S pressure is increased the sample becomes dark and brittle. Therefore, the selection of an optimum processing temperature was necessary. Long periods of vacuum annealing results in a shift of the Fermi level towards the conduction band due to an increase in the concentration of V_S defects, and the conduction property in changed to n-type in the surface region of the crystal. Vacuum annealing reduces the resistivity to the same extent as does sulfur annealing, although only a slight change of color was observed.

3.2 $CuAlS_2$ and metal contact

The current-voltage characteristics of various metal-$CuAlS_2$ contacts were studied. Most of the junctions show a high-resistivity ohmic contact. Among them, the Al-$CuAlS_2$ contact exhibited Schottky junction properties. Figure 1 shows the I-V characteristic of the Schottky junction measured at room temperature. Of all the etching solutions studied, HF was found to be the most effective in providing a clean surface of $CuAlS_2$. Results of X-ray photoelectron spectroscopy suggested that oxygen contamination at the surface of $CuAlS_2$ was most effectively reduced by HF etching. Etching for 30 s in HF solution in combination with the Al and Au contact can give the best rectification characteristics. HF etching for longer than 30 s causes a rough surface and poor rectification. After repeated studies, we finally found that reproducible results can be obtained in as-grown crystals rather than in vacuum-annealed ones.

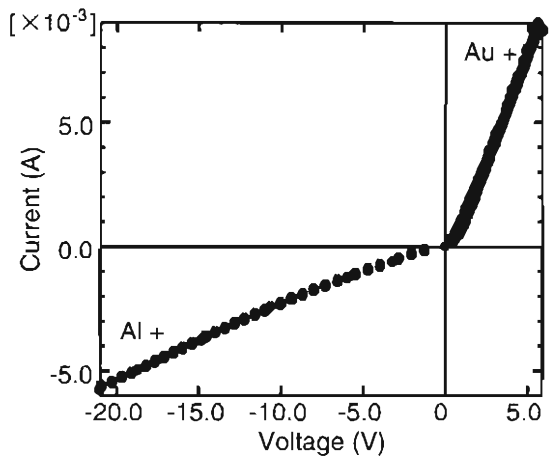

Fig. 1. Current-voltage characteristics of Al-$CuAlS_2$-Au diode.

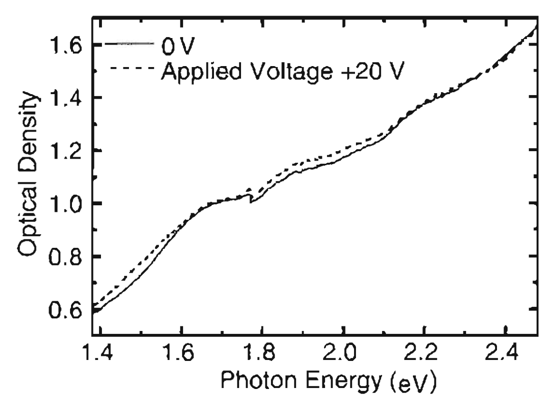

Fig. 2. Absorption spectra of Al-$CuAlS_2$-Au diode. Straight curve: without bias. Dotted curve: with forward bias of 20 V.

3.3 Absorption spectra of $CuAlS_2$

Absorption spectra of the MS diode of Al-$CuAlS_2$-Au at 20 K are shown in Fig. 2. The spectrum without electric field is plotted as a straight curve. Application of the forward-bias voltage of 20 V to the junction causes an increase in the absorption coefficient for a certain wavelength region. In contrast, no change of the spectrum occurs for a reverse-bias. Application of the voltage causes this change instantaneously. Stopping the voltage immediately restores the initial spectrum. The time constant for the change is very small although it has not been quantitatively measured. The difference in absorption spectra for with and without application of voltage is shown in Fig. 3. In this figure, two broad peaks are observed at 1.5 and 1.9 eV. The former peak is narrower than the latter. The change in optical density amounted to 0.04. Some diodes show a greater change of optical density amounting to 0.2 in

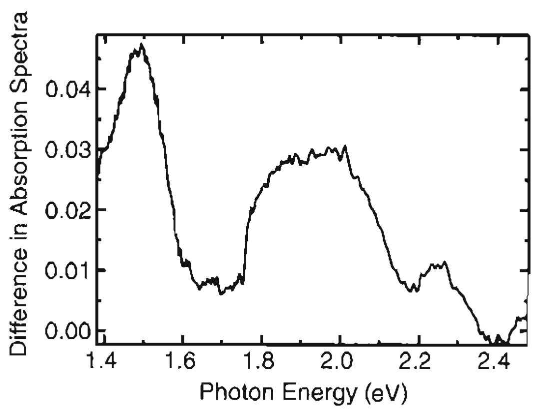

Fig. 3. Difference in absorption spectra with and without application of voltage.

the 1.5 eV region. (Change of the absorption coefficient was about 20 cm^{-1}.) We believe that the change in spectra around 1.9 eV is related to the Fe impurity, since peaks of Fe^{3+}-related charge-transfer-type absorption have been observed at 1.1 and 1.9 eV in $CuAlS_2$.[7] Application of the forward-bias voltage may cause a downward shift of the Fermi level across the Fe^{2+}/Fe^{3+} demarcation level, which leads to an increase in the relative concentration of Fe^{3+}. On the contrary, no TA-related absorption bands have been reported in the 1.5 eV region. We suspect that the latter absorption may be related to some kind of charged states introduced by the formation of the Schottky contact. Details on the absorption are still under investigation.

4. Conclusions

We have prepared a MS diode using an Al-$CuAlS_2$ contact and successfully changed the absorption spectra by applying forward-bias voltage. We believe that the change is caused by an electrically induced downward shift of the Fermi level across the demarcation levels of Fe^{2+}/Fe^{3+} and/or some other charged states.

Acknowledgements

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