Change of Optical Absorption by Application of Electric Field in Al-$CuAlS_2$-Au Diode

Takao Nishi*, Naohiro Ishibashi, Naoyuki Hayashi, Chihomi Furuhashi and Katsuaki Sato†

Faculty of Technology, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184-8588, Japan。

Planer type Schottky-type metal-semiconductor diodes were prepared using $CuAlS_2$ single crystal with evaporated metal contacts of Al and Au. It is found that optical absorption spectra can be changed by application of the electrical field to the Al-$CuAlS_2$-Au diode. This change in the absorption is attributed to the change in the valence of the transition atom impurities due to the movement of Fermi level caused by electric field.

KEY WORDS: $CuAlS_2$, Schottky diode, electrically induced change of absorption

1. Introduction

Wide gap chalcopyrite type crystals have been known to undergo a change of color of the crystals by deviation from stoichiometry[1)] or doping of impurities.[2)] We have been working with optical properties of $CuAlS_2$ doped with transition atom (TA) impurities and revealed that valence state of transition atoms (TA) can be changed by sweeping the Fermi level across the demarcation levels for the individual TA (such as Fe^{2+}/Fe^{3+}, Cr^{+}/Cr^{2+}).[3)] This effect of Fermi level motion induces change of optical absorption spectrum in TA doped $CuAlS_2$, which leads to a change of color in the crystal. From theses experiments we have been convinced that the color of the chalcopyrite crystal can be artificially controlled not only by the thermal treatments but also by electronic perturbation. In the present work, an artificial control of the absorption spectrum of $CuAlS_2$ by application of the electrical field is studied. In order to move the Fermi level position by application of the electric field, we tried to make a Schottky metal-semiconductor (MS) type diode. However, only a few reports have been published on 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 Al-$CuAlS_2$:Mn contact as a DC red EL device.[5)] These works are only for luminescent devices and no MS diodes aiming at electrical control of absorption have been investigated.

Systematic studies on fabrication of MS contacts to the $CuAlS_2$ single crystals have not been conducted. However, since all as-grown $CuAlS_2$ single crystals obtained by chemical transport exhibit p-type conductivity with the resistivity higher than 10^4 Ωcm and the hole mobility lower than 3 $cm^2V^{-1}s^{-1}$, it is therefore very difficult to form a good contact to this material. Moreover, no information on the surface properties of $CuAlS_2$ was available. We therefore started studies of measurement of work functions. We systematically investigated MS junctions for $CuAlS_2$ single crystals, changing metals (Al, Au, Yb, Ag, In), etchants (HF, HNO_3, HCl, H_2SO_4 and $K_2Cr_2O_7$) and time duration for etching.

2. Experimental

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 stoichiometry elements or the powder of polycrystalline $CuAlS_2$ compound prepared by the direct melting of constituent elements in a PBN crucible held in a sealed quartz ampoule.[6)] The resulting $CuAlS_2$ single crystals typically had dimensions of about $1\times3\times5$mm^3. As-grown crystals are highly compensated showing very high resistivity of one MΩcm order. In order to reduce the resistivity, annealing of crystals in the vacuum or sulfur atmosphere was performed. The sample was put into a silica ampoule and sealed in vacuum of 1×10^{-6} Torr. For sulfur(S)-annealing, the temperature was kept at 800℃ for 24 h, while for vacuum(V)-annealing, the temperature was kept at 800℃ for a few weeks. After the thermal annealing in sulfur atmosphere the $CuAlS_2$ crystal was rinsed in a boiling CS_2 solution to remove the sulfur adhered on the surface. The thermal treatment in sulfur atmosphere decreases 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. Long time vacuum annealing shifts Fermi level towards the conduction band due to an increase in the concentration of V_s-defects, and changes the conduction property to n-type in the surface region of the crystal. The vacuum-annealing reduces the resistivity to the same extent as the sulfur annealing.

We started studies of measurement of work functions. From photoemission studies, the work function ϕ of as-grown and sulfur-annealed $CuAlS_2$ (p-type) was determined to be 3.6 eV and 4.3 eV, respectively. Taking into account the energy band gap (3.5 eV) of this semiconductor, the measured values of ϕ suggest strong bending of the energy bands at the surface. Therefore, it is clear that surface treatment has a crucial importance if one wants to form a good Schottky barrier.

We systematically investigated metal-semiconductor (MS) junctions for $CuAlS_2$ single crystals, changing metals, etchants and time duration for etching. The crystals were mirror-polished and etched in different chemical solutions for different time duration to remove the damaged surface layers or surface oxides formed on the crystals, and rinsed in deionized water. We used HF, HNO_3, HCl, H_2SO_4, and $K_2Cr_2O_7$ solutions for the chemical treatments. The etching times of 30sec, 1min, and 5min (more 10min and 20min for H_2SO_4) were tried. Planar-type metal-semiconductor (MS)-diodes were prepared. Two metal contacts were alternately evaporated on the surface of the single crystals with a spacing of about 1 mm. Contact metals we investigated were Au, Al, Ag, In and Yb.

** E-mail: takawou@cc.tuat.ac.jp

† To whom reprint requests should be addressed

Thin wire contacts were soldered to metal electrodes using an In solder to apply voltage to the diode placed in a cryostat. Absorption spectra were measured at 20K by using a tungsten lamp as a light source. The 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). The spectrograph system displays optical absorption spectra in the spectral range between 500 and 900nm for a shutter-opening period of two seconds. Background subtraction and blank measurement for absorbance were also performed using built-in software. Absorption spectra with and without application of electrical field to the diode were measured.

3. Results and discussion

The results of electrical measurements for all the MS diodes prepared under different surface treatments are summarized in Table 1. Of all the etching solutions studied, HF was found by ESCA to be the most effective to remove the oxidized surface layer providing the clean surface of $CuAlS_2$. The 30-s etching in HF solution and combination of Al and Au contact can give the best rectification characteristics. An HF etching for longer than 30 s causes a rough surface and a bad rectification. Only the Al-$CuAlS_2$ contact with 30 second HF treatment of $CuAlS_2$ resulted in Schottky-like current-voltage characteristics as described in our preceding paper.[7)]

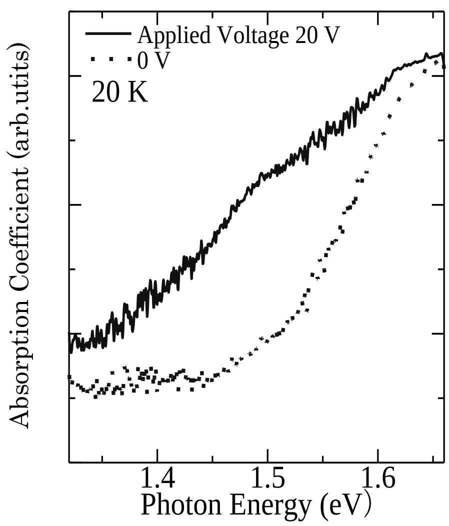

Fig. 1 Electrically induced change of absorption spectrum in Al-$CuAlS_2$ contact

Absorption spectra were measured at 20K with the light focused on the Al-$CuAlS_2$ contact area in the MS diode employing a vacuum-treated $CuAlS_2$ crystal. The spectra with and without electric field are plotted in Fig. 1 by dotted and straight curves, respectively. Application of the forward bias voltage of 20 V to the junction causes an increase in the absorption coefficient for a certain wavelength region. On the contrary, application of the reverse bias results in no change of the spectrum. No detectable change of spectrum was observed when the light was focused on Au-semiconductor contact area. This change occurs instantaneously after the voltage is applied. Release of the voltage also restores immediately the initial pectrum.

We consider that the change of spectra is related to the transition metal impurity, since peaks of Fe^{3+}-related charge-transfer type absorption has been observed between 1.1 and 1.9 eV in $CuAlS_2$.[8)] Application of the forward bias voltage may cause a downward shift of the quasi Fermi level across the Fe^{2+}/Fe^{3+} demarcation level, which leads to an increase in the relative concentration of Fe^{3+}. We believe that the change should have occurred in less than milliseconds, although no transient measurements have been studied. Transient measurements are now underway.

4. Conclusion

In conclusion, we have shown in this paper that we have prepared a MS diode using Al-$CuAlS_2$ contact and successfully changed the absorption spectra by application of forward 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+}.

Table 1 Electrical properties of metal-$CuAlS_2$ junction for different metals and different surface (Ω: ohmic, △: poorly rectifying, ○: rectifying, ◎: well rectifying, ＊: unreliable, shadow: no data)

Etchants	Period	Au/Al	Au/Ag	Au/In	Au/Yb-
Br+mehanol	1min	Ω			
	5min	＊			
H_2SO_4	30sec	＊	△	Ω	
	1min	△	△	Ω	
	5min	△			
	10min	○			
	20min	○			
HCl	30sec	Ω			
	1min	△			
	5min	△			
$K_2Cr_2O_7$ +H_2SO_4	30sec	＊			
	1min	＊			
	5min	Ω			
HF	30sec	◎	△	Ω	
	1min	△	△	Ω	
	5min	Ω			
HNO_3	30sec	Ω		Ω	
	1min	Ω		Ω	
	5min	Ω	Ω	Ω	Ω

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