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# Characterization of Novel Cu-Al-Se Films Grown by MBE

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Undoped and Zn-doped Cu-Al-Se films have been grown on GaAs(100) substrates by molecular beam epitaxy, and their optical and electrical properties have been characterized. The compositions are about 50at%Cu, 10at%Al and 40at%Se. Photoluminescence spectrum of an undoped film exhibits a blue emission. The undoped and Zn-doped films show p-type and n-type conductivity, respectively. These characteristics suggest the possibility of p-n junction optical devices. The current-voltage characteristic of ZnSe/undoped Cu-Al-Se/ p-GaAs exhibits a rectifying characteristic with the turn-on voltage of 2.7 V.

## 1. Introduction

One of chalcopyrite structure compounds, $CuAlSe_2$, has a direct band gap of 2.7 eV, and its optical and electrical properties have been studied for bulk materials.[1-4] We succeeded in the epitaxial growth of the stoichiometric $CuAlSe_2$ film by molecular beam epitaxy (MBE), the photoluminescence spectrum of which, however, showed deep level-related emissions.[5] MBE is a nonequilibrium growth technique allowing the fabrication of a Cu-Al-Se phase different from the chalcopyrite structure.[6] Recently, we have grown novel Cu-Al-Se films with noticeable optical and electrical properties. The photoluminescence spectrum of this film exhibits a blue emission at 77K and R.T. The Hall measurements of the undoped and Zn-doped samples show p-type and n-type conductivity, respectively. We report here on the characterization of novel Cu-Al-Se films grown by MBE, and discuss the possibility of p-n junction optical devices fabricated with the undoped and Zn-doped Cu-Al-Se films. On the other hand, one of II-VI compounds, ZnSe, has a direct band gap of 2.7 eV, and tends to be n-type. We also propose another possibility of p-n heterojunction fabricated with the p-type Cu-Al-Se and n-type ZnSe films.

## 2. Experimental

The source materials used in this work were 6N purity, elemental Cu, Al, Se and Zn, and GaAs (100) substrates were used. The growth of the Cu-Al-Se films were practiced at 600 °C using K-cells for Cu, Al, Se and Zn sources. An undoped Cu-Al-Se film with the thickness of 0.9 $\mu$m was grown under the condition of the Cu K-cell temperature at 1160 °C for 1.5h as the second stage subsequent to the growth at 1050 °C for 0.5h as the first stage. This two-stage growth method enhances the film quality greatly. Next, a Zn-doped film was grown under the same condition as that of the above sample, except using the K-cell for Zn source set at 190 °C. Each K-cell temperature for Al and Se sources was set at constant temperatures of 1100 °C and 210 °C, respectively, in both cases. The background pressure during growth was around $10^{-9}$ Torr. These grown films were characterized by inductively coupled plasma (ICP) mass spectrometry, X-ray diffraction, transmission electron microscopy (TEM), photoluminescence, and Hall measurement by the van der Pauw technique. For the Hall measurement, ohmic contacts were made using In metal. Next, we have grown the undoped Cu-Al-Se film subsequent to the Zn-doped Cu-Al-Se film on n-type GaAs substrate. Current-voltage characteristics were measured. Lastly, we have grown a ZnSe film subsequent to the undoped Cu-Al-Se film on p-type GaAs substrate. For the ZnSe growth, the growth temperature was set at 400 °C.

## 3. Results and discussion

The result of ICP mass spectrometry showed the mean composition of the undoped Cu-Al-Se film grown to be 50at%Cu, 10at%Al and 40at%Se, which is considerably different from the stoichiometry of the chalcopyrite structure compound $CuAlSe_2$. This composition can be described as the formula of $Cu_5AlSe_4$, which satisfies the charge neutrality condition.

Compounds with this compositional ratio exist in the Cu-Fe-S and Cu-In-Se systems. It is possible that the compound of $Cu_5AlSe_4$ may exist in the Cu-Al-Se system.

According to the result of X-ray diffraction, diffraction peaks appear at $2\theta = 31.7°$ and 66.1° corresponding to (200) and (400) reflections of the GaAs substrate, and at $2\theta = 32.9°$ and 68.9° corresponding to reflections of the film. Assuming that the crystal structure of the grown film is equivalent to the zincblende type structure, the grown crystal is oriented with its a-axis perpendicular to the substrate surface, and its lattice constant, a, is calculated to be 0.545 nm. This agrees with half the lattice constant, c/2, of the tetragonal chalcopyrite compound $CuAlSe_2$ (a = 0.560 nm, c = 1.090 nm).

Fig. 1 shows the TED patterns with the incident beam along the <110 > azimuth of the undoped film. Fig.1(a) and 1(b) correspond to areal parts near the film/substrate interface and film surface, respectively. The diffraction pattern of fig.1(a) shows a single crystalline phase with some twins. This is true across much wider or different regions than in fig.1(a). Thus, it is revealed that the film has grown epitaxially on the GaAs substrate. Fig.1(b) shows the pattern of a single crystalline phase with scarcely any twins. However, the existence

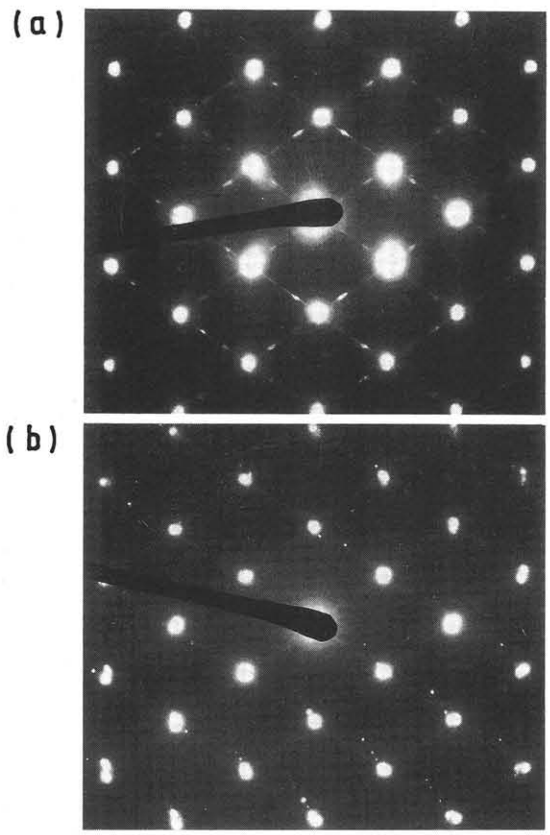


Fig.1 Electron diffraction patterns of undoped Cu-Al-Se film with the incident beam along <110> azimuth : (a) near the substrate and (b) near the surface.

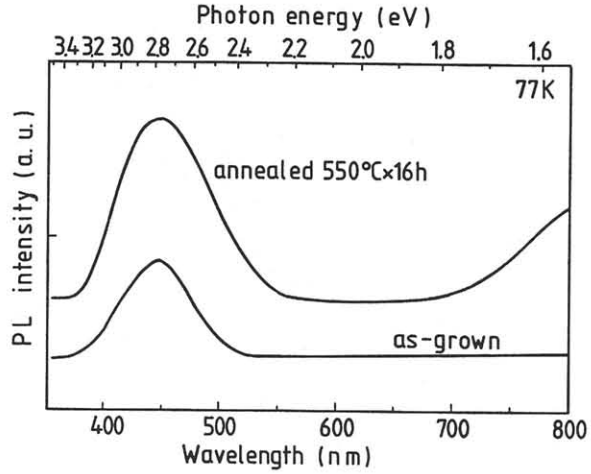


Fig.2 Photoluminescence spectra at 77K of as- grown and annealed undoped Cu-Al-Se films.

of additional double spots in Fig.1(b) suggests that this film near the surface contains single crystal domains tilting slightly with respect to each other. It is concluded that the Cu-Al-Se film has grown epitaxially on the substrate, however, the crystalline structure contains some defects which decrease with the film thickness.

Fig. 2 shows the photoluminescence spectra at 77K of the as-grown and annealed at 550 °C for 16h films for the undoped sample. The spectrum of the as-grown film exhibits the blue emission in the wavelength range from 380nm to 520nm, which is the near band edge emission. The band gap of the film is calculated to be above 3.3 eV, corresponding to the wavelength of 380nm. The annealing at 550 °C for 16h caused the blue emission to become stronger with accompanying deep level-related emissions. Photoluminescence of the above films is visible as a blue light even at room temperature. Though fig.2 seems to show the appearance of a new phase, there remains unresolved possibility of coexistence of $CuAlSe_2$ and $Cu_2Se$. This point should be clarified later. On the other hand, the photoluminescence at 77K for the Zn-doped sample has shown no emission, probably because of a poor crystalline quality.

Hall measurements of the undoped sample annealed at 550 °C showed stable p-type conductivity. Variations of the conductivity with the annealing time are shown in fig.3. As the annealing time increases, the resistivity decreases notably, the carrier concentration increases greatly, and the mobility increases gradually. The sample annealed for 16h showed the resistivity of $6.9 \times 10^{-2}\ \Omega\cdot cm$, the carrier concentration of $2.5 \times 10^{18}\ cm^{-3}$ and the mobility of 370 $cm^2 \cdot V^{-1} \cdot s^{-1}$, which were remarkably of

good quality. On the other hand, the as-grown Zn-doped film exhibited n-type conductivity with the resistivity of 2.1 x$10^{-3}$ Ω·cm, the carrier concentration of 1.9 x$10^{19}$ $cm^{-3}$ and the mobility of 150 $cm^2 \cdot V^{-1} \cdot s^{-1}$.

Fig.4 shows the current-voltage characteristic of the layered structure of undoped/Zn-doped Cu-Al-Se films/n-GaAs annealed at 550 °C for 16h. Though the characteristic exhibits the formation of a diode, the turn-on voltage is very small compared with the wide band gap of the Cu-Al-Se film. Zn is one of the dopants for the p-type GaAs. A p-n junction may be formed within the GaAs substrate because of Zn diffusion from the Zn-doped Cu-Al-Se film. We

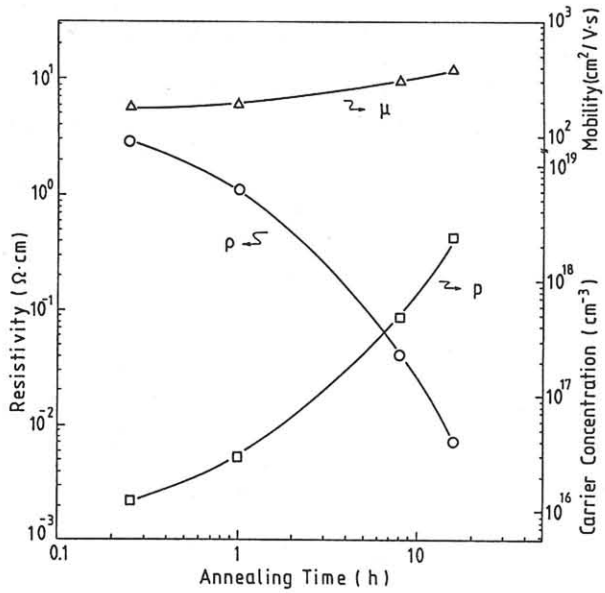


Fig.3 Variations of electrical properties of undoped sample annealed at 550 °C with annealing time.

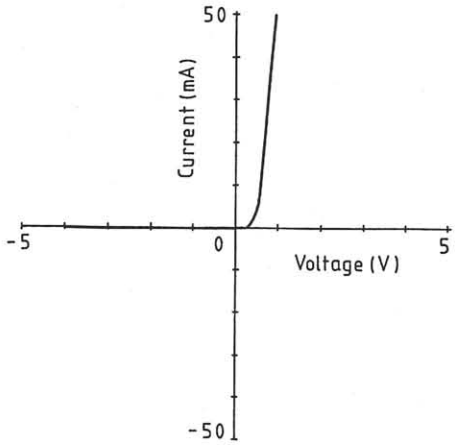


Fig.4 Current-voltage characteristic of undoped/Zn-doped Cu-Al-Se/n-GaAs at R.T.

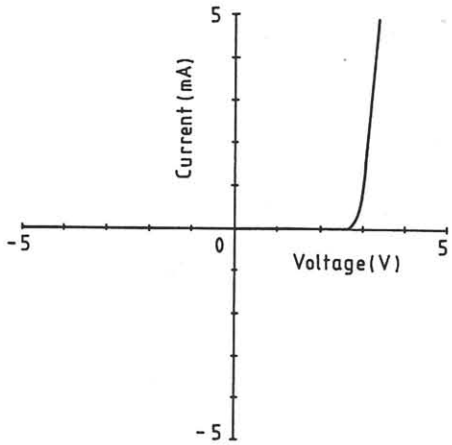


Fig.5 Current-voltage characteristic of ZnSe/undoped Cu-Al-Se/p-GaAs at R.T.

should examine the electrical properties of the Zn-doped Cu-Al-Se in details. Fig.5 shows the current-voltage characteristic of ZnSe/undoped Cu-Al-Se/p-GaAs. Fig.5 exhibits a rectifying characteristic with the turn-on voltage of 2.7V, and suggests the formation of a p-n heterojunction.

In summary, novel Cu-Al-Se films were grown by MBE, and their optical and electrical properties were characterized. The compositions are about 50at%Cu, 10at%Al and 40at%Se. Photoluminescence spectrum of an undoped film exhibited a blue emission at 77K and room temperature. Hall measurements of the undoped and Zn-doped samples showed the p-type and n-ype conductivity, respectively. The epitaxial film of Cu-Al-Se on GaAs substrate could be grown, though its crystalline quality was not so good. The results obtained up to the present suggest the possibility of p-n junction optical devices fabricated with these novel Cu-Al-Se films.

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