Preparation of Copper(Cu) Thin Films by MOCVD and Their Conversion to Copper Selenide (CuSe) Thin Films through Selenium Vapor Deposition

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Recently, the preparation of copper selenide thin film has attracted much attention of particular interest due to their wide applications such as electronic and electro-optical devices.[1-3] In the literature, various copper selenides with different compositions, including stoichiometric Cu_2Se, Cu_3Se_2, CuSe and $CuSe_2$, and nonstoichiometric $Cu_{2-x}Se$ were well-characterized and documented in addition to their phase transformations.[4,5] Typical preparation methods for these films include vacuum evaporation of Cu_2Se at the high temperature above 1000 °C[6a] and chemical bath deposition at 50 °C.[6b] But the latter method was reported to have difficulties in controlling film thickness, conductivity, and grain size. In our laboratory, the preparation of CuSe thin film was considered to be an important intermediate process in the context of its use as a precursor material as well as InSe for the preparation of $CuInSe_2$ thin films that can be applied to high efficiency solar cell.[7] Thus, copper thin films was first prepared by metal organic chemical vapor deposition method (MOCVD) using organometallic precursors and then they were converted to copper selenide thin films through selenium vapor deposition. In this study, bis(ethyl butyrylacetato)copper(II), (designated as $Cu(ebac)_2$), and bis(ethyl isobutyrylacetato)copper(II), (designated as $Cu(eiac)_2$) were synthesized by reacting $CuCl_2$ and corresponding sodium salts of β-diketonates at room temperature. The products were very stable in ambient condition and were easily characterized by IR, mass spectroscopy, and elemental analysis. In thermogravimetry and differential scanning calorimetry(TG/DSC) under argon atmosphere, they were found to have relatively low melting endotherm at about 100 °C and multistep decomposition processes, as summarized below;

precursor	color	melting point (°C)	onset temp. of decomposition (°C)
$Cu(ebac)_2$	blue-green	104	196
$Cu(eiac)_2$	dark green	98	206

The major components of gas mixture from the decomposition processes were easily identified to be ethanol, CO_2, and acetaldehyde on the basis of known gas phase IR spectra. MOCVD experiments were carried out without H_2 gas using the two Cu(II) precursors in a glass warm-wall reactor with silicon or glass substrates. Substrate temperature was controlled to 310-350 °C range and feed temperature to 90-110 °C range. Working pressure during deposition was maintained at about 1 Torr using argon for flowing gas. Adhesion of the Cu films to the substrates was good, but it should be mentioned that in case of $Cu(ebac)_2$ precursor, no deposition on silicon substrate was observed. Deposition rate was about 12.5 Å/min. Average resistivities of the Cu films by four point probe method was 1.699 $\mu\Omega\cdot$cm, indicating that the film is composed of very pure copper metal, and this result was corroborated by X-ray diffraction pattern(JCPDC 4-836) as shown in Figure 1.

Also, XPS (VG Scientific Ltd., ESCALAB MK-11) analysis revealed that there are no appreciable amounts of impurities such as C or O. Scanning electron micrographs of the copper film deposited using $Cu(eiac)_2$ as a precursor showed that the morphology of the deposited films depends on the substrate temperature and the deposition time; as the temperature and time increase, the grain size increases. For instance, the average size of the grains in copper films on Si wafer substrate grown at 290 °C was about 0.15 μm, but increased to about 1.5 μm when they were grown at 370 °C as shown in Figure 2.

The experiments for the transformation of Cu thin films to copper selenides through selenium vapor deposition were

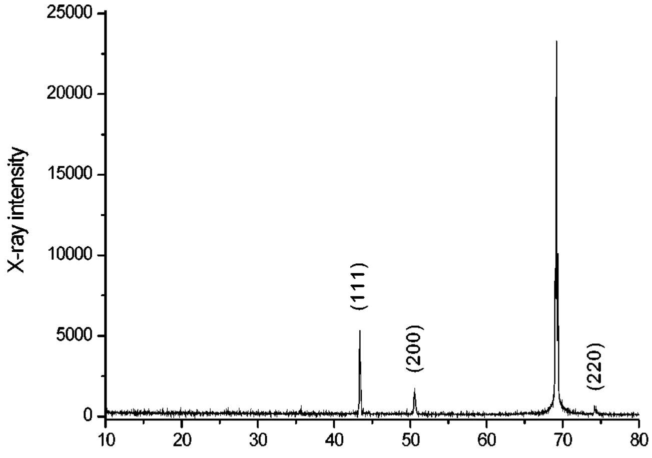
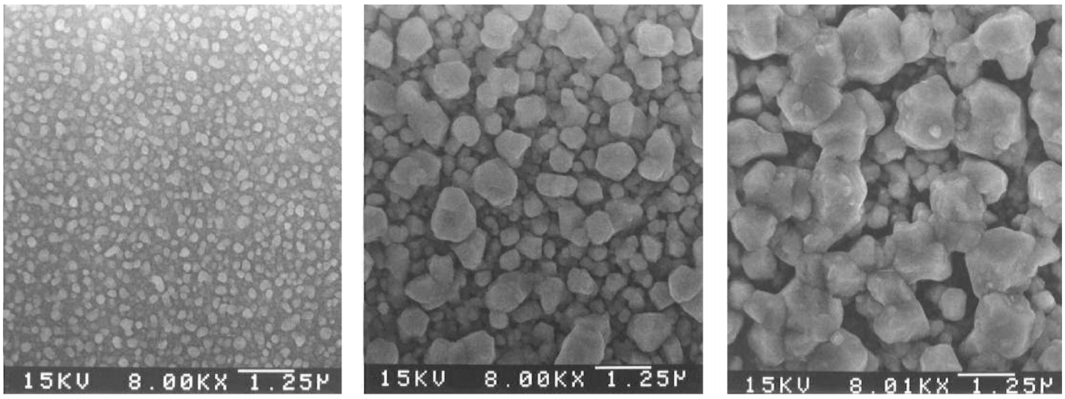


Figure 1. X-ray diffraction pattern of copper film deposited on Si substrate.



(a) 290 ℃ (b) 330 ℃ (c) 370 ℃

Figure 2. SEM micrographs of copper films at different substrate temperatures.

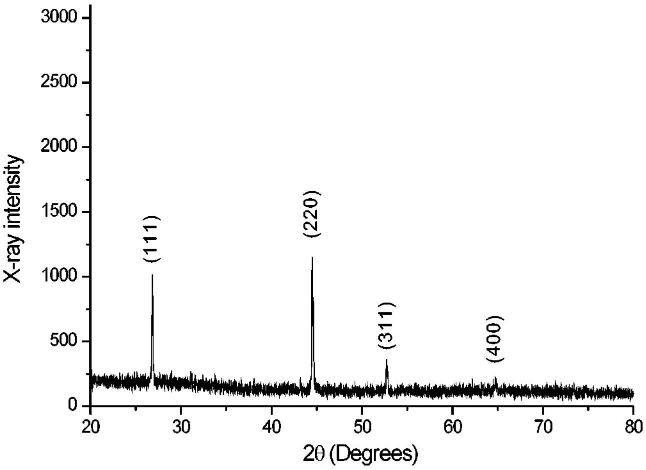


Figure 3. XRD pattern of $Cu_{2-x}Se$ obtained after annealing in vacuum for 1 h at 250 °C.

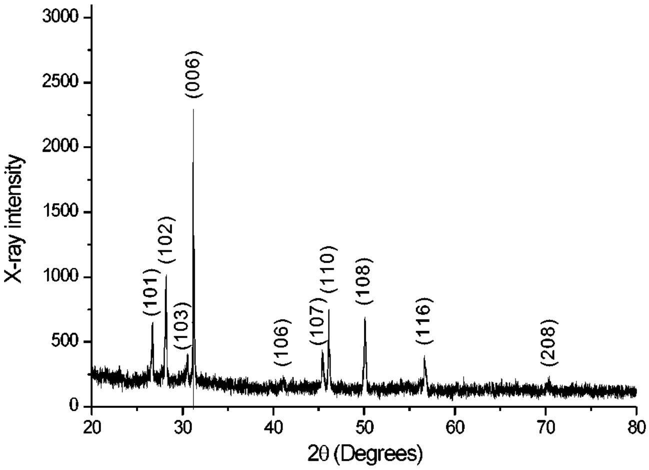


Figure 4. XRD pattern of CuSe obtained after annealing in Ar for 1 h at 150 °C.

implemented by simply exposing the copper thin film to selenium vapor at 250 °C. After 4 hours, the copper metallic color of the films changed to black and the X-ray diffraction pattern of the resulting films accords quite well with that of $Cu_{2-x}Se$ (JCPDS 6-680) as shown in Figure 3. Further exposure of the resulting $Cu_{2-x}Se$ films to selenium vapor at 250 °C for 8 hours converted them to CuSe (JCPDS 34-171) thin film, as shown in Figure 4.

It is interesting to note that no other peaks from Cu_3Se_2, $CuSe_2$, and Cu_7Se_4 appeared in the XRD patterns, although the reason is not clear at this stage. On heating those CuSe thin films on glass substrates in argon gas (50 mTorr) or in vacuum at 400 °C for 4 hours, they transform back to $Cu_{2-x}Se$.

In conclusion, very pure copper thin film was successfully prepared by MOCVD using new organometallic Cu(II) precursors and characterized. Also, it was proved that the resulting copper films could be transformed to $Cu_{2-x}Se$ or to CuSe thin films by selenium vapor deposition method at relatively mild conditions.

General Methods

Infrared spectra were obtained on Jasco FT/IR-5300 spectrometer and NMR spectra were recorded on Varian Gemini 2000 NMR spectrometer. Elemental analyses were performed with EA-1110 Fisous and thermal analyses including TGA and DSC were carried out with Setaram LABSYS. Mass spectra were obtained on Autospec EBE mass spectrometer. $Cu(ebac)_2$ was synthesized by reacting 0.2 mol of ethyl butyrylacetate and NaOH, and 0.1 mol of $CuCl_2$ (Aldrich Chem. Co.) in a 30 mL solution of 95% methanol at room temperature. After 2 hours, the solvent was evaporated and resulting residue was dissolved in a pentane solution. The solution was filtered off to remove impurities and the product was obtained after evaporation of the pentane solvent. Final product was recrystallized in pentane solution and/or sublimated right before each CVD experiment. **$Cu(ebac)_2$**: IR (KBr pellet, cm^{-1}): 2983 (m), 2960 (m), 2931 (m), 2872 (w), 1596 (s), 1529 (s), 1368 (w), 1302 (s), 1258 (s), 1172 (m), 1054 (m), 978 (w), 776 (s), 503 (w); Mass (70 eV, *m/e*): 377, 34%, $[^{63}Cu(ebac)_2]^+$; 379, 18%, $[^{65}Cu(ebac)_2]^+$; elemental analysis: calcd. C: 50.85%, H: 6.93 %; found. C: 48.44%, H: 6.85%. **$Cu(eiac)_2$** was similarly prepared using corresponding ethyl isobutyrylacetate and sodium metal in THF soution as above. $Cu(eiac)_2$: IR (KBr pellet, cm^{-1}): 2971 (m), 2932 (m), 2872 (w), 1606 (s), 1586 (s), 1534 (s), 1509 (s), 1366 (m), 1326 (s), 1263 (s), 1178 (m), 1093 (m), 1045 (s), 954 (m), 797 (m), 492 (m), 469 (m); Mass (70 eV, *m/e*): 377, 89%, $[^{63}Cu(eiac)_2]^+$; 379, 58%, $[^{65}Cu(eiac)_2]^+$; elemental analysis: calcd. C: 50.85%, H: 6.93%; found. C: 51.24%, H: 7.32%.

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