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Structural studies of copper sulfide films: effect of ambient atmosphere

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Abstract

We examined the structural properties of copper sulfide films as a function of the sulfurization time of 70-nm-thick Cu films. Copper sulfide films with various phases such as mixed metallic Cu-chalcocite, chalcocite, roxbyite, and covellite phases were formed with increasing sulfurization time. To evaluate the structural stability of various films, all the films were exposed to the ambient atmosphere for the same amount of time. Although the phase structure and stoichiometry of the films were maintained at a greater depth, the near-surface region of the films was oxidized and covered with overlayers of oxide, hydroxide, and/or sulfate species due to the exposure and reaction with the ambient atmosphere. The oxygen uptake and its reactivity with the copper sulfide film surfaces were enhanced with increasing sulfur content of the films. In addition, the type of divalent state of copper formed on the film surfaces depended on the phase structure, composition, and stoichiometry of the films.

Keywords: copper sulfide, x-ray photoelectron spectroscopy, x-ray diffraction

1. Introduction

Copper sulfide, a p-type semiconductor, has recently attracted considerable scientific and technological interest as a promising material with potential applications in solar cells, optical filters, nanoswitches, thermoelectric and photoelectric transformers, and gas sensors [1–6]. In addition to the technological interest, copper sulfide is an important material from the point of view of fundamental research. Because of the effect of the 3*d* electrons, this transition-metal compound has the ability to form various stoichiometries, of which at least five phases are stable at room temperature [7, 8]. Such varying stoichiometries and valence states greatly affect the structural, optical, and electrical properties of copper sulfide. Thus, the stoichiometry, structure, and phase composition of copper sulfide films used for device fabrication should be precisely controlled, which will depend on the preparative conditions used for the film deposition. The ability to grow tailor-made copper sulfide films is an important goal in current material development and device fabrication at the nanoscale. Also, the growth of high-quality films without any contamination is essential for the optimum efficiency of devices fabricated using these films. In fact, solid-source molecular beam epitaxy using a sulfur valved cracker effusion cell (VCC), which is used to evaporate high-vapor-pressure materials in ultrahigh vacuum (UHV), is a promising method for the sulfurization of Cu films [9, 10]. This evaporation technique uses elemental sulfur, thereby avoiding not only the conventional problems associated with the handling of metalorganics but also the possibility of contamination due to the use of compound source materials.

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It is also imperative to understand the structural stability of grown copper sulfide films because the chemical or physical environment may affect the valence states of the material [11], which could result in modified film properties with a direct affect on the effectiveness of the films used in device fabrication and/or application. Since the operation of a device is usually carried out under ambient atmospheric conditions, it is important that the copper sulfide films retain their original structure and stoichiometry under ambient environmental conditions.

In this paper, we report the growth of various phases of copper sulfide films by the sulfurization of Cu films grown on Si(001) substrates for different times using a sulfur VCC under UHV conditions. In addition we also report on the effect of ambient atmospheric conditions on the structural stability of various films. We carried out a systematic investigation by x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and x-ray-initiated Auger electron spectroscopy (XAES) to evaluate the phase and structural properties of such copper sulfide films.

2. Experiment

The growth of copper sulfide films on Si(001) substrates was carried out in a UHV deposition system. N-type Si(001) samples ($20 \times 20 \times 0.5\,mm^3$) were chemically cleaned in a $H_2SO_4 : H_2O_2$ solution and rinsed in deionized water. After the sample was introduced into the treatment chamber of the deposition system, a clean Si(001) surface was obtained by heating the sample at 1100 °C for 2–3 min [12]. The sample was then transferred into the metal deposition chamber of the system, which was equipped with a Knudsen cell that served as a source of copper. A 70-nm-thick Cu film was deposited on the clean Si(001) substrate at room temperature, where the film thickness was monitored using a quartz crystal microbalance. The sample was finally transferred into the sulfur deposition chamber that was connected to a sulfur VCC. The bulk evaporator of the VCC that held the sulfur-source crucible was heated at 135 °C. The cracking zone of the VCC was kept at 900 °C to convert sulfur from a polyatomic form to simpler species through thermal pyrolysis, and thereby enhance the reactivity of the sulfur species with the Cu film [9]. Sulfur was introduced into the UHV chamber at a pressure of 2×10^{-6} Torr using a needle valve located between the crucible and the cracking zone, and the substrate was kept at 75 °C. To assess the dependence of the structural properties of the copper sulfide films on the sulfurization time, we fabricated several films by the sulfurization of various 70-nm-thick Cu/Si(001) samples for 10, 20, 25, and 35 min. To assess the effect of ambient conditions on the structural stability of the grown films, all the films were exposed to ambient atmospheric conditions for 48 h prior to carrying out characterization.

The chemical composition and structural properties of the copper sulfide films were analyzed by *ex situ* XRD, XPS, and XAES. The XRD patterns of various films were recorded using Cu$K\alpha$ radiation on a Rigaku RINT 2500 VHF x-ray diffractometer operated at 40 kV and 450 mA. The diffractometer was equipped with a thin film attachment, where we used a glancing angle of 3° and recorded the XRD patterns in the selected angular range of 20–52°. XPS investigations were performed with Al$K\alpha$ as the x-ray radiation using a Physical Electronics PHI 5800 ESCA system. The photoelectrons were detected at a takeoff angle of $\phi = 25°$ with respect to the surface normal. The sampling information depth (ID) of the photoelectrons was calculated using the formula $\mathrm{ID} = 3\lambda\cos\phi$, where λ is the inelastic mean free path of the photoelectrons in the films [13, 14]. ID was estimated as 5.2 nm for S 2p photoelectrons by assuming $\lambda_{S\,2p} = 1.9$ nm in copper sulfide [13, 14]. XAES investigations were performed using the same instrument as that used for the XPS studies. Al$K\alpha$ radiation was also used as the x-ray source and the Auger electrons were detected at a takeoff angle of $\phi = 25°$ with respect to the surface normal.

3. Results and discussion

3.1. Phase structure characterization: XRD analysis

Figure 1 shows the XRD patterns of the copper sulfide films formed by the sulfurization of 70-nm-thick Cu films on Si(001) substrates for various times. It is seen from the XRD patterns that the films were crystalline in nature with narrow peaks indicating large grain sizes. All the peaks in the XRD pattern for the sample sulfurized for 10 min could be indexed as the monoclinic chalcocite Cu_2S phase (JCPDS file 83-1462) [15]. The XRD pattern of this sample also exhibited peaks due to unreacted metallic Cu with 111 and 200 reflections (JCPDS file 04-0836). In fact, the peak intensity of the metallic Cu 111 reflection was the strongest in the XRD pattern. This indicated that a substantial amount of the initial Cu film remained unreacted when the sulfurization process was terminated after only 10 min. The sample sulfurized for 20 min exhibited a pure monoclinic chalcocite Cu_2S phase with no metallic Cu peaks, which indicated that the underlying unreacted Cu film was completely converted into the chalcocite Cu_2S phase. A change in the phase structure was observed for the sample sulfurized for 25 min, for which all the peaks in the XRD pattern could be indexed as the monoclinic roxbyite Cu_7S_4 phase (JCPDS file 23-0958) [16]. The sample sulfurized for 35 min exhibited a further change in the phase structure; all the peaks in the XRD pattern could be indexed as the hexagonal covellite CuS phase (JCPDS file 06-0464) [17]. Thus, the XRD results indicated the formation of various copper sulfide phases depending on the sulfurization time of the initial Cu film. Note that although the initial 70-nm-thick Cu films deposited on the Si(001) substrate grew with preferred orientation along the (111) and (200) planes, we did not observe a significant preferential orientation along any planes for the various copper sulfide films formed by the sulfurization of the initial Cu films.

3.2. Film composition and chemical environment: XPS analysis

Figure 2 shows the S 2p XPS core-level spectra of the copper sulfide films obtained by sulfurization of the initial Cu films

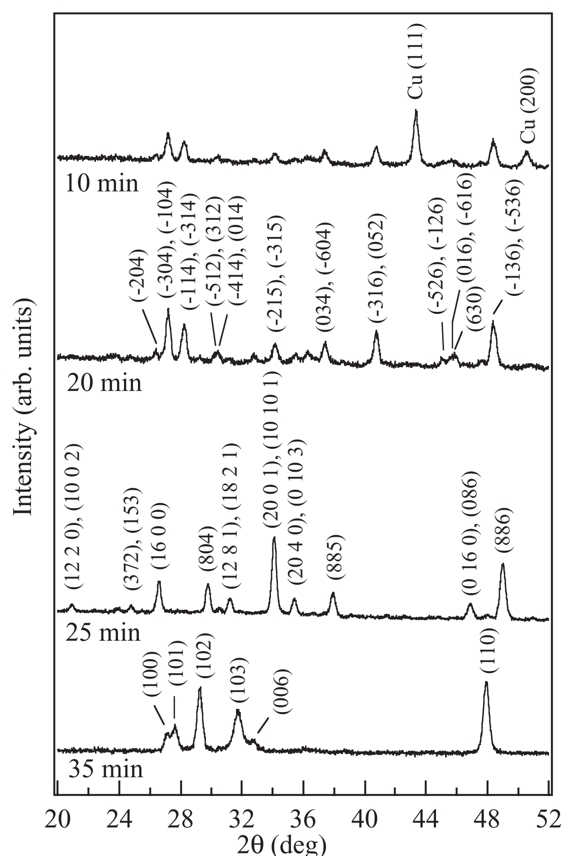

Figure 1. XRD patterns of copper sulfide films obtained by sulfurization of 70-nm-thick Cu films on Si(001) substrates for various times.

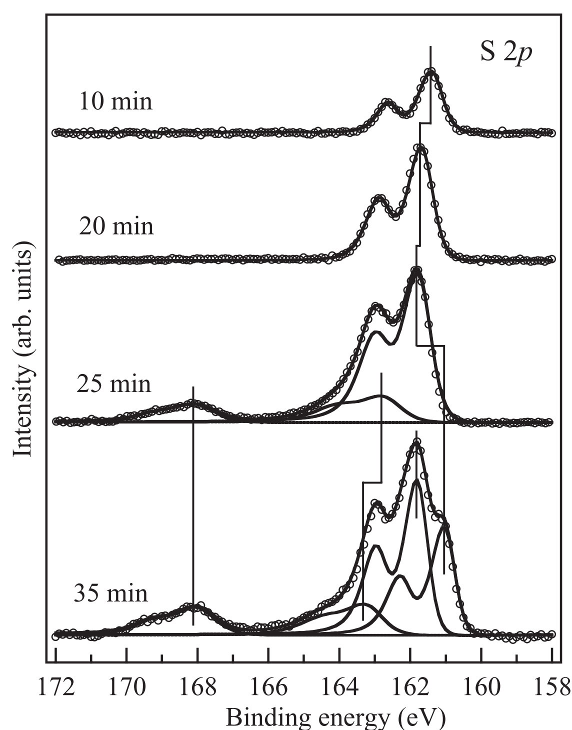

Figure 2. S 2*p* XPS spectra of copper sulfide films formed by sulfurization of initial Cu films for various times. The dark solid lines in the spectra represent the fitted peaks.

for various times. In all the cases, peak fitting for the S 2*p* line shapes was performed using a Gaussian–Laurentzian product function with a spin orbit splitting of 1.2 eV while keeping the intensity ratio I(S $2p_{3/2}$) : I(S $2p_{1/2}$) at 2 : 1 [14]. For the sample sulfurized for 20 min, peak fitting indicated the presence of a well-defined doublet species with the S $2p_{3/2}$ binding energy located at 161.7 eV. This observed binding energy clearly indicated the existence of a Cu–S–Cu bonding configuration and agreed well with the S $2p_{3/2}$ binding energy reported for sulfur in stoichiometric chalcocite Cu_2S [14, 18]. For the sample sulfurized for 10 min, although peak fitting revealed the presence of a well-defined doublet species, the binding energy of the S $2p_{3/2}$ peak was observed at 161.4 eV, which was located about 0.3 eV lower than that of the sample sulfurized for 20 min. This binding energy shift of the S $2p_{3/2}$ peak towards a lower value indicated a different chemical environment for the Cu film that was sulfurized for 10 min, where the sulfur species are more likely to experience a Cu-rich environment than in the sample sulfurized for 20 min. This fact, coupled with the electronegativity values, can be used to explain this chemical shift. Since the electronegativity of S is much higher than that of Cu (S - 2.5 and Cu - 1.9), the electron cloud around S should be denser for the sample sulfurized for 10 min. Thus, the core hole created due to photoionization in the core level of S is expected to be more screened, thereby causing a decrease in the binding energy.

For the sample sulfurized for 25 min, peak fitting of the S 2*p* spectrum revealed the presence of three doublets, i.e. a well-defined doublet, a shoulder doublet, and a weak doublet at a higher binding energy. The binding energy of the S $2p_{3/2}$ peak of the well-defined doublet was observed at 161.8 eV, which agreed well with the S $2p_{3/2}$ binding energy reported for sulfur in roxbyite Cu_7S_4 [19]. This is consistent with the results of our XRD phase structure analysis. Note that this binding energy was 0.1 eV higher than that of the chalcocite Cu_2S in the sample sulfurized for 20 min. This suggested that the sulfur species of the film experienced a more S-rich chemical environment. The binding energy of the S $2p_{3/2}$ peak of the shoulder doublet was observed at 162.8 eV. This doublet was attributed to the presence of a highly Cu-deficient nonstoichiometric sulfide (∼17.4% of the S 2*p* total peak area) in the film [19, 20]. The binding energy of the S $2p_{3/2}$ peak of the additional weak doublet was observed at 168.15 eV. This doublet was attributed to the presence of a sulfate species (SO_4^{2-}) overlayer (∼11.1% of the S 2*p* total peak area) on the film due to the oxidation of the film surface [19, 21, 22].

Peak fitting of the S 2*p* spectrum for the sample sulfurized for 35 min revealed the presence of two well-defined doublets, a shoulder doublet, and a weak doublet at a higher binding energy. The two well-defined doublets indicated the presence of two different binding states of sulfur in the sample. The binding energies of the S $2p_{3/2}$ peak of the two well-defined doublets were 161.03 and 161.8 eV, which agreed well with the S $2p_{3/2}$ binding energies reported for sulfur in covellite CuS [23, 24]. The covellite phase is represented by the formula $Cu_3^+(S_2)^{2-}S^-$, where two-thirds of the sulfur atoms

form S_2 groups while one-third of the sulfur atoms (S_B) are isolated [23, 24]. The S $2p_{3/2}$ peak located at 161.03 eV corresponded to the isolated sulfur atoms (planar sulfur) and the peak located at 161.8 eV corresponded to S_2 units (sulfur in S–S bonds) [23, 24]. Furthermore, the observed S_B $2p_{3/2}$ peak position of 161.03 eV was 0.67–0.77 eV lower than that of the chalcocite (161.7 eV) obtained after 20 min sulfurization and roxbyite (161.8 eV) obtained after 25 min sulfurization. This is because the geometrical distances of planar Cu–S_B in covellite CuS are much shorter than the Cu–S distances in chalcocite Cu_2S and other copper sulfides containing S^{2-} [23]. The binding energy of the S $2p_{3/2}$ peak of the shoulder doublet was observed at 163.28 eV and was attributed to the presence of a highly Cu-deficient nonstoichiometric sulfide (∼13.4% of the S $2p$ total peak area) in the film. The binding energy of the S $2p_{3/2}$ peak of the additional weak doublet was observed at 168.15 eV and was attributed to the presence of a sulfate species (SO_4^{2-}) overlayer (∼11.9% of the S $2p$ total peak area) on the film surface.

Figure 3 shows the Cu $2p_{3/2}$ XPS core-level spectra of the copper sulfide films formed by sulfurization of the initial Cu films for different times. Nonlinear backgrounds were removed from the spectra using a method described by Sherwood [25]. Nonlinear least-squares curve fitting was performed using a Gaussian-Laurentzian peak shape with a spin orbit splitting of 1.6 ± 0.1 eV [26, 27]. For the sample sulfurized for 20 min, peak fitting indicated the presence of a well-defined peak with the Cu $2p_{3/2}$ binding energy located at 932.7 eV. This energy agreed well with the Cu $2p_{3/2}$ binding energy reported for the monovalent state of copper [Cu(I)] in chalcocite Cu_2S [18, 28, 29]. For the sample sulfurized for 10 min, peak fitting also revealed the presence of a well-defined Cu $2p_{3/2}$ peak with the binding energy located at 932.7 eV, which indicated the presence of a chalcocite phase. However, the XRD pattern (figure 1) for this sample indicated the presence of a mixed metallic Cu-chalcocite-phase film. This showed that the Cu $2p$ XPS core-level spectrum was not sufficiently sensitive to distinguish between the monovalent [Cu(I)] and metallic [Cu(0)] states of copper in our sample because of the similar binding energies of these two states [30]. For the sample sulfurized for 25 min, peak fitting revealed the presence of a well-defined peak with the Cu $2p_{3/2}$ binding energy located at 932.5 eV, which agreed well with the Cu $2p_{3/2}$ binding energy reported for the monovalent state of copper in roxbyite Cu_7S_4 [20]. Note that this binding energy was 0.2 eV lower than that of the chalcocite Cu_2S in the sample sulfurized for 20 min. This indicated that the Cu species of the film experienced a more S-rich chemical environment. Peak fitting for the sample sulfurized for 35 min revealed a further shift in the binding energy of the Cu $2p_{3/2}$ peak towards a lower value. The Cu $2p_{3/2}$ binding energy was located at 932.35 eV, which agreed well with the Cu $2p_{3/2}$ binding energy reported for the monovalent state of copper in covellite CuS [28, 29]. However, note that the S $2p$ spectrum (figure 2) clearly indicated the presence of two well-defined doublet peaks, i.e. two different binding states of sulfur in the covellite

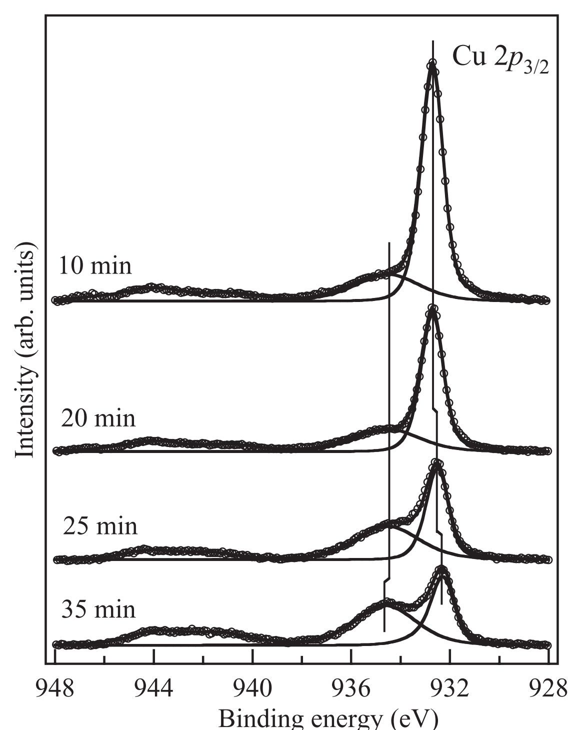

Figure 3. Cu $2p_{3/2}$ XPS spectra of copper sulfide films formed by sulfurization of initial Cu films for various times. The dark solid lines in the spectra represent the fitted peaks.

film obtained by 35 min sulfurization. In fact, peak fitting of the Cu $2p_{3/2}$ spectrum for bulk covellite by Laajalehto *et al* revealed the presence of two peaks that indicated the presence of two binding states of copper separated from each other by 1.2 eV (932.35 eV and 933.55 eV) [28], where both the binding states represented the formal oxidation state +1. In our case, the second copper peak in the Cu $2p_{3/2}$ spectrum for the sample sulfurized for 35 min overlapped with the divalent state of copper [Cu(II)], and was difficult to distinguish and deconvolute from the divalent state.

Next, we discuss the presence of the divalent state of copper [Cu(II)] in the copper sulfide films. Peak fitting of the Cu $2p_{3/2}$ spectra clearly revealed the presence of an additional component at a higher binding energy for all the samples (figure 3). This additional peak was observed at a binding energy of 934.46 eV for the samples sulfurized for 10, 20, and 25 min, and at a binding energy of 934.63 eV for the sample sulfurized for 35 min. In addition, a weak satellite shake-up band structure was observed in the Cu $2p_{3/2}$ spectra for all the samples at approximately 940–945 eV. This presence of the additional component peak at the higher binding energy in the Cu $2p_{3/2}$ spectra accompanied by the weak satellite structure indicated the presence of the divalent state of copper [Cu(II)] in the copper sulfide films [19, 22, 23]. These results indicated that exposure of the copper sulfide films to the ambient atmosphere for 48 hours caused their surfaces to oxidize and form the divalent state of copper [Cu(II)]. The surfaces of the mixed metallic Cu-chalcocite film obtained after 10 min sulfurization and the pure chalcocite film obtained after 20 min sulfurization

were covered with a cupric oxide and/or copper hydroxide species overlayer, where the observed binding energies of the additional component peak in the Cu $2p_{3/2}$ spectra agreed well with the binding energies reported for the divalent state of copper [Cu(II)] in cupric oxide and copper hydroxide [27, 31, 32]. Note that while the S $2p$ spectra (figure 2) for the samples sulfurized for 10 and 20 min did not show any evidence of sulfate species (SO_4^{2-}) on the film surfaces, the spectra for the samples sulfurized for 25 and 35 min clearly indicated its existence. Furthermore, only about 11.1 and 11.9% of the S $2p$ total peak area (figure 2) corresponded to the sulfate overlayer for the samples sulfurized for 25 and 35 min, respectively. However, figure 3 shows that as much as 52.3 and 57.3% of the Cu $2p_{3/2}$ total peak area corresponded to the divalent state of the copper [Cu(II)] overlayer after 25 and 35 min, respectively. This indicated that the surfaces of the roxbyite film obtained after 25 min and the covellite film obtained after 35 min were covered with an overlayer that was not a pure copper sulfate species but consisted of a mixture of copper sulfate, cupric oxide, and copper hydroxide species, where the observed binding energies of the additional component peak in the Cu $2p_{3/2}$ spectra (figure 3) coincided with the binding energies reported for the divalent state of copper [Cu(II)] in copper sulfate [19, 21, 22, 27] as well as cupric oxide and copper hydroxide [27, 31, 32]. However, it was difficult to perform a detailed quantitative analysis of the amount of copper sulfate, cupric oxide, and copper hydroxide species present in the overlayers due to the similar and overlapping binding energies of the divalent state of copper [Cu(II)] in the Cu $2p_{3/2}$ spectra for these species. Thus, our results indicated that the type of divalent state of copper [Cu(II)] formed on the surfaces of the copper sulfide films depended on the phase structure and stoichiometry of the films. It is interesting to note that the XRD results (figure 1) did not show evidence of the presence of the divalent state of copper [Cu(II)] in any of the copper sulfide films. Since XPS is sensitive to the near-surface region (~5 nm), while XRD provides information from a greater depth of the film, the comparison of XRD and XPS results indicated that although various phases of copper sulfide films could be grown precisely, the exposure to the ambient atmosphere caused the surfaces of all the films to oxidize and form Cu oxide, hydroxide, and/or sulfate species overlayers in the divalent state.

Figure 4 shows the plot of the (divalent Cu(II)/total Cu $2p_{3/2}$) peak area ratio for the copper sulfide films as a function of the sulfurization time of the initial Cu film. All the samples were exposed to the ambient atmosphere for the same amount of time (48 h) before carrying out characterization. However, it can be clearly seen that the amount of the divalent state of copper [Cu(II)] formed on the surfaces of the copper sulfide films varied considerably and depended on the film phase structure and composition. The amount of divalent copper present on the film surfaces increased with increasing sulfurization time, i.e. with increasing sulfur content of the films. Thus, the amount of the divalent state of copper formed on the surface of the mixed metallic Cu-chalcocite film obtained after 10 min sulfurization was lowest, whereas it

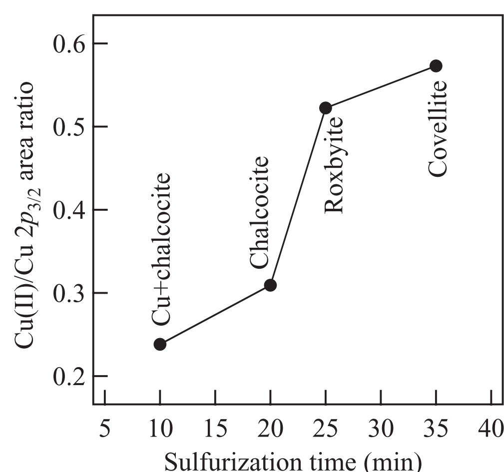

Figure 4. Divalent Cu(II)/total Cu $2p_{3/2}$ peak area ratio for various copper sulfide films as function of sulfurization time of the initial Cu film.

was greatest on the surface of the covellite film obtained after 35 min sulfurization. These results indicated that the oxygen uptake and its reactivity with the copper sulfide film surfaces to form oxide, hydroxide, and/or sulfate overlayers were enhanced with increasing sulfur content of the films.

Figure 5 shows the XAES spectra of the Cu $L_3M_{45}M_{45}$ transition for the copper sulfide films. The Cu $L_3M_{45}M_{45}$ Auger feature was found to be more sensitive to the various copper sulfide phases than the core-level Cu $2p_{3/2}$ peak. This is because the relaxation effect is more pronounced in the doubly ionized state of the Auger process than in the singly ionized state of the photoelectron process [33]. For the pure chalcocite film obtained after 20 min sulfurization, the Cu $L_3M_{45}M_{45}$ peak was observed at a kinetic energy of 917.05 eV, which agreed well with the kinetic energy reported for the chalcocite phase [18, 21, 29, 33]. For the mixed metallic Cu-chalcocite film obtained after 10 min sulfurization, the Cu $L_3M_{45}M_{45}$ peak was observed at a kinetic energy of 917.05 eV, and the peak position was the same as that after 20 min sulfurization. Thus, no clear distinction in the kinetic energies of the Auger peak position for copper in chalcocite Cu_2S and that for metallic Cu [Cu(0)] could be made in our samples. For the roxbyite film obtained after 25 min, the Cu $L_3M_{45}M_{45}$ peak was observed at a kinetic energy of 917.82 eV, which agreed well with the kinetic energy reported for the roxbyite phase [20]. For the covellite film obtained after 35 min, the Cu $L_3M_{45}M_{45}$ peak was observed at a kinetic energy of 918.15 eV, which agreed well with the kinetic energy reported for the covellite phase [21, 29, 33]. The Cu $L_3M_{45}M_{45}$ peak positions for the samples sulfurized for 25 and 35 min were 0.77 and 1.1 eV higher than that for the sample sulfurized for 20 min, respectively. Thus, the Cu $L_3M_{45}M_{45}$ kinetic energy chemical shifts for the copper sulfide films were consistent with the Cu $2p_{3/2}$ core level binding energy shifts (figure 3) for the corresponding films. However, we note a greater separation in the Cu $L_3M_{45}M_{45}$ Auger peak positions for the films compared with the Cu $2p_{3/2}$ core-level photoelectron

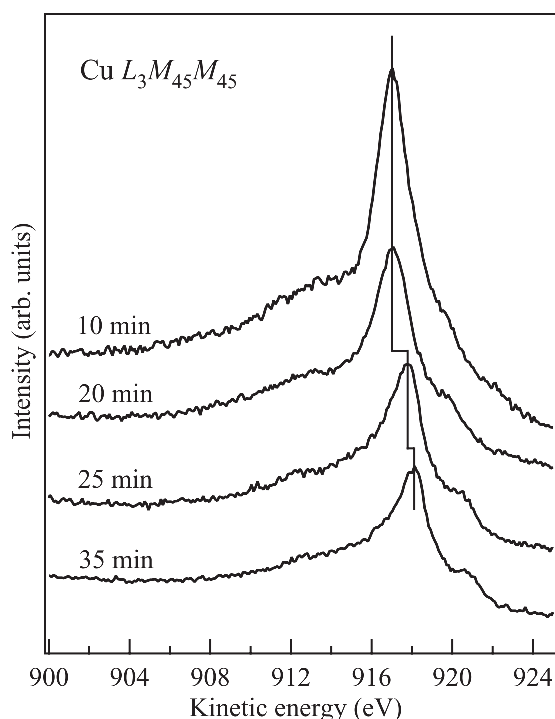

Figure 5. XAES Cu $L_3M_{45}M_{45}$ transition for copper sulfide films formed by sulfurization of initial Cu films for various times.

spectra, an observation that is useful for detailed analysis with the aim of differentiating various copper sulfide phases spectroscopically.

4. Conclusions

We grew copper sulfide films by the sulfurization of 70-nm-thick Cu films on Si(001) surfaces under UHV conditions. Films with various phase structures such as mixed metallic Cu-chalcocite, chalcocite, roxbyite, and covellite phases were obtained by varying the sulfurization time. All the films were exposed to the ambient atmosphere for the same amount of time (48 h) before performing XRD and XPS characterization. Although XRD studies did not show any evidence of the presence of oxide, hydroxide, and/or sulfate species in any of the copper sulfide films, XPS results clearly indicated their existence. This indicated that although the phase structure and stoichiometry of the films were maintained at a greater depth of the films, the near-surface region of the films was oxidized due to exposure to the ambient atmosphere, and the films were covered with overlayers consisting of copper compounds with copper in the divalent state [Cu(II)]. Furthermore, the oxygen uptake and its reactivity with the copper sulfide surfaces were enhanced with increasing sulfur content of the films. In addition, the type of divalent state of copper [Cu(II)] formed on the film surfaces depended on the phase structure, composition, and stoichiometry of the films. Thus, for the fabrication of devices such as nanoscale switches, sensors, and solar cells, chalcocite-phase films would be more suitable than roxbyite- and covellite-phase films. This is because the roxbyite- and covellite-phase films have higher sulfur content than the chalcocite-phase film; they therefore oxidize and degrade faster under ambient atmospheric conditions thereby rendering devices, fabricated using these phases, unreliable over time.

References

[1] Grozdanov I and Najdoski M 1995 *J. Solid State Chem.* **114** 469
[2] Dachraoui M and Vedel J 1987 *Sol. Cells.* **22** 187
[3] Mattox D M and Sowell R R 1974 *J. Vac. Sci. Technol.* **11** 793
[4] Setkus A, Galdikas A, Mironas A, Simkiene I, Ancutiene I, Janickis V, Kaciulis S, Mattongo G and Ingo G M 2001 *Thin Solid Films* **391** 275
[5] Sakamoto T, Sunamura H, Kawaura H, Hasegawa T, Nakayama T and Aono M 2003 *Appl. Phys. Lett.* **82** 3032
[6] Banno N, Sakamoto T, Hasegawa T, Terabe K and Aono M 2006 *Japan J. Appl. Phys.* **45** 3666
[7] Okamoto K and Kawai S 1973 *Japan J. Appl. Phys.* **12** 1130
[8] Chakrabarti D J and Laughlin D E 1986 *Binary Alloy Phase Diagrams* ed T B Massalski (Metals Park, OH: American Society of Metals) p 953
[9] Arthur J R 2002 *Surf. Sci.* **500** 189
[10] Terabe K, Hasegawa T, Nakayama T and Aono M 2005 *Nature* **433** 47–50
[11] Nakai I, Sugitani Y, Nagashima K and Niwa Y 1978 *J. Inorg. Nucl. Chem.* **40** 789
[12] Swartzentruber B S, Mo Y W, Webb M B and Lagally M G 1989 *J. Vac. Sci. Technol.* A **7** 2901
[13] Seah M P and Dench W A 1979 *Surf. Interface Anal.* **1** 2
[14] Contini G, Laajalehto K, Suoninen E and Marabini A M 1995 *J. Colloid Interface Sci.* **171** 234
[15] Evans H T Jr 1971 *Nat. Phys. Sci.* **232** 69
[16] Mumme W G, Sparrow G J and Walker G S 1988 *Mineral. Mag.* **52** 323
[17] Gadgil S B, Thangaraj R and Agnihotri O P 1986 *Thin Solid Films* **145** 197
[18] Deroubaix G and Marcus P 1992 *Surf. Interface Anal.* **18** 39
[19] Lefevre G, Bessiere J, Ehrhardt J J and Walcarius A 2003 *J. Environ. Radioact.* **70** 73
[20] Laajalehto K, Kartio I and Nowak P 1994 *Appl. Surf. Sci.* **81** 11
[21] Galtayries A and Bonnelle J P 1995 *Surf. Interface Anal.* **23** 171
[22] Griffis D P and Linton R W 1982 *Surf. Interface Anal.* **4** 197
[23] Folmer J C W and Jellinek F 1980 *J. Less-Common Met.* **76** 153
[24] Pattrick R A D, Mosselmans J F W, Charnock J M, England K E R, Helz G R, Garner C D and Vaughan D J 1997 *Geochim. Cosmochim. Acta* **61** 2023
[25] Sherwood P M A 1983 *Practical Surface Analysis by Auger and Photoelectron Spectroscopy* ed D Briggs and M P Seah (London: Wiley) p 445
[26] Sherwood P M A 1990 *Data Analysis in XPS and AES in Practical Electron Spectroscopy* Appendix 3 ed D Briggs and M P Seah (New York: Wiley) p 555
[27] Rossi A, Atzei D, Da Pelo S, Frau F, Lattanzi P, England K E R and Vaughan D J 2001 *Surf. Interface Anal.* **31** 465
[28] Laajalehto K, Kartio I, Kaurila T, Laiho T and Suoninen E 1996 *Proc. 6th Eur. Conf. Appl. Surf. Interface Anal. ECASIA'95* ed B Reihl and D Briggs (New York: Wiley) p 717
[29] Kuhn M and Rodriguez J A 1994 *J. Phys. Chem.* **98** 12059
[30] Wang S and Yang S 2001 *Mater. Sci. Eng.* C **16** 37
[31] Watanabe M, Tomita M and Ichino T 2002 *J. Electrochem. Soc.* **149** B97
[32] Cano E, Lopez M F, Simancas J and Bastidas J M 2001 *J. Electrochem. Soc.* **148** E26
[33] Perry D L and Taylor J A 1986 *J. Mater. Sci. Lett.* **5** 384