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S. Seal

University of Central Florida

L. Bracho

University of Central Florida

S. Shukla

University of Central Florida

J. Morgiel

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Processing and characterization of nanometer sized copper sulfide particles

S. Seal,^{a)} L. Bracho, and S. Shukla

Advanced Materials Processing Analysis Center (AMPAC), and Mechanical,
Materials & Aerospace Engineering (MMAE), University of Central Florida, Orlando, Florida 32816

J. Morgiel

Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 25 Reymonta Street,
30-059 Krakow, Poland

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Nanomaterials have attracted considerable attention in modern-day technology. In this article, sulfide nanoparticles of industrial interest are formed by the sol-gel process using metal chloride precursors dissolved in a mixture of silica gel and organic cellulose network followed by a chemical reaction with hydrogen sulfide gas. Particles are then heated in a vacuum oven. While scanning and transmission electron microscopy are used to study their morphology and structure in the nanometer scale, x-ray photoelectron spectroscopy is employed to understand the bonding chemistry and the stoichiometry of the sulfide particles as a function of H₂S exposure and heat treatment. The results from this study are expected to show promising applications and production of other oxides, sulfides and their compounds using sol-gel synthesis are indicated. © 1999 American Vacuum Society. [S0734-2101(99)10005-8]

I. INTRODUCTION

During the past decade, nanomaterials have attracted considerable interest in technological revolution. The physico-chemical as well as magnetic and optical properties of nanomaterials are very different from their bulk because the particle size diameters are less than the Bohr exciton radius.¹ Nanoparticles hold a promising future in electronics; as precursors for building components of the chips or for development of new photocells and sensors, or for generating very small active elements in magnetic recording.² This has promoted the development of various processing techniques, such as the sol-gel process,³ chemical vapor deposition,⁴ and electrochemical and chemical processing with organometallic precursors.⁵ Besides processing, an intensive characterization of nanoparticles using scanning electron microscope (SEM), transmission electron microscope (TEM, for determining the particle size), x-ray diffraction (XRD, for determining the crystalline nature of the particles), and x-ray photoelectron spectroscopy (XPS, for determining the chemical states, stoichiometry of the films and other chemical species in the matrix) is needed to understand the material behavior in nanophase.

Due to high surface reactivity, synthesizing nanoparticles, however, pose real challenges because of their agglomeration. Sol-gel synthesis offers a great degree of control of the atomic composition and structure at the molecular level, which is unachievable with traditional sintering or precipitation methods. Since the chemistry and microstructure of the solid determine its properties, this technology can be used to design materials with specified mechanical, optical, electronic, and physicochemical properties.⁶ Nanosized particles,

such as CdS, PbS, ZnS, Fe₂O₃, produced by the sol-gel technique have been reported.⁷⁻⁹

The present article reports the processing and characterization of CuS nanoparticles dispersed in hydroxypropyl cellulose (HPC)-silica films with the gas diffusion method. CuS is a potential material for lubricant and solar cells based on cadmium sulfides. Metal precursors are dissolved in the matrices and converted to nanoparticles by chemical reaction. It is to be noted in our experiments that HPC, an organic polymer with OH groups, facilitates the formation of a homogeneous organic-polymer silica film for fine dispersion of a Cu-metal precursor for CuS production.

II. EXPERIMENT

A. Materials processing

HPC, CuCl₂, AlCl₃, HCl, TEOS (tetraethyl orthosilicate) were purchased from Aldrich Chemicals, USA. The proce-

FIG. 1. Calculated solubility limit of copper chloride as a function of HPC and silica content. The point C is our chosen composition (includes the AlCl₃ addition) for nanoparticle processing.

^{a)}Electronic mail: sseal@pegasus.cc.ucf.edu

(a)

(b)

FIG. 2. Optical micrographs of CuS particles, (a) freshly prepared and (b) with time (network formation): Mag: 1000 $\times$.

cedure for preparation of HPC-silica films containing CuS nanoparticles is described below. A dipping solution for preparation of the CuS precursor films was prepared by dissolving CuCl_2 , AlCl_3 , and silica sol in 100 ml of methanol containing 0.5 gm of HPC.

The silica sol was prepared from hydrolysis of TEOS by dissolving 10 g of TEOS in a mixture of water, methanol (anhydrous), and hydrochloric acid (35%). A homogeneous mixture of silica sol solution was prepared after stirring the mixture for half an hour. Excessive stirring leads to hardening of the silica sol and makes it unusable.

Chosen metal precursor films were formed on glass plates by the dip drying method at room temperature. The plates (roughened for better adhesion) were dipped (once) in the solution for 1–2 min and were dried for 3–4 min(s) before H_2S exposure. The nanophase CuS dispersed films were obtained by exposing the precursor films to H_2S for 2–5 s followed by heating in a vacuum furnace (1×10^{-4} Torr) at 150–180 $^\circ\text{C}$ for 1 h. The conversion of CuCl_2 to CuS is

(a)

(b)

FIG. 3. SEM micrographs of CuS particles, (a) freshly prepared (nanometer sized) and (b) with time (network formation, particle growth and cluster).

indicated by a change in film color from light yellowish to blue during H_2S exposure.

B. Particle morphology

The particle size distribution was studied using an optical microscope and JEOL scanning electron microscope (SEM). The nanometer size sulfide particles were further characterized by transmission electron microscope Philips CM200FEG. The sample was ion milled in argon from one side of the glass plate at 4 kV.

C. Surface chemical characterization

The nanoparticle sulfide films produced on glass plates were characterized by a 5400 PHI ESCA (XPS) spectrometer having a base pressure of 10^{-10} Torr using $\text{Al K}\alpha$ X radiation (1486 eV, linewidth 0.7 eV) with a power of 350 W. Survey and individual high-resolution spectra were recorded with a pass energy of 44 and 17 eV to achieve the maximum instrument resolution. The binding energy of the gold ($4f_{7/2}$) at 84 ± 0.2 eV was used to calibrate the binding energy scale of the spectrometer. Any charging shifts produced by the

FIG. 4. TEM micrographs of CuS dispersed particles with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{HPC}/\text{silica sol}/\text{AlCl}_3$, (a) uniformly distributed nanoparticles and (b) twinning of CuS particle.

samples were removed by using a binding energy scale referenced to C(1s) binding energy of the hydrocarbon part of the adventitious carbon line at 284.6 eV.¹⁰ Nonlinear backgrounds were removed from the spectra using a method described by Sherwood.¹¹ Nonlinear least-squares curve fitting was performed using a Gaussian/Lorentzian peak shape,^{11,12} after background removal using a method described in the literature.¹¹ The peak heights and areas under the peaks have been used to measure the relative atomic concentrations.

III. RESULTS AND DISCUSSIONS

A. Role of hydroxypropyl cellulose

Particle size distribution is greatly affected by the inhomogeneous distribution of Cu^{+2} ions in CuCl_2 containing matrix. HPC, a cellulose derivative, is one of the effective polymeric matrix for uniform distribution of metal precursors in the soluble matrix. Since CuS is produced by the H_2S gas diffusion, the diffusion of Cu^{+2} ions controls the particle growth. The polymeric sol-gel network is believed to suppress the CuS particle growth. The diffusion of H_2S gas into the matrix is responsible for copper sulfide reaction only. Moreover, HPC forms a molecular hybrid with silica via hydrogen bonds through its hydroxyl and ether groups.¹³ This allows HPC to act as a compatibilizer for uniform dispersion of CuCl_2 in the silica matrix to a molecular level for producing nanometer sized particles. The XPS Si (2p) binding energy in silica gel is found to be 102.7 eV (less than that of Si in silica ~ 103.2 eV), indicating an enhanced covalency in the Si(2p) character in the polymeric network.

B. Effect of metal precursor solubility

The calculated solubility of metal precursor (CuCl_2) in the HPC containing polymeric matrix is dependent on the silica and HPC content (see Fig. 1). CuCl_2 crystals precipi-

TABLE I. Selected XPS core-level binding energies (± 0.1 eV) of CuS nanoparticles processed via metal precursor and gas diffusion method. Reference binding energy C(1s)=284.6 eV.

	C(1s)	Cu(2p) _{3/2}	S(2p) _{3/2} / (2p) _{1/2}	Cl(2p) _{3/2} / (2p) _{1/2}	Si(2p)
No H ₂ S/ no heat	C-H (L) C-O-C (L) C-OH (L) C=O (S)	933.6 CuO 934.9 CuCl ₂	...	199.9/202.2 CuCl ₂ 198.4/200.4 AlCl ₃	103.2 SiO ₂ (L) 102.5 (S)
FWHM		(2.6 eV)		(3.4 eV)	(2.5 eV)
H ₂ S/no heat	C-H (L) C-O-C (L) C-OH (M)	931.6 CuS 932.5 CuCl (?)	161.5/162.7 CuS	198.3/200.4 AlCl ₃ (L)	102.5
FWHM		(2.3 eV)	(2.9 eV)	(2.9 eV)	(1.9 eV)
H ₂ S/heat	C-H C-O-C (M) C-OH (S) C=O (S)	931.6 CuS C=O (S)	161.6/162.8 CuS	198.3/200.4 AlCl ₃ (L)	102.6
FWHM		(1.9 eV)	(3.0 eV)	(2.8 eV)	(1.8 eV)

^aNote: () total full width half maximum, L=large, M=medium, S=small (XPS peak intensity).

FIG. 5. XPS deconvoluted $\text{Cu}(2p_{3/2})$ spectra for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ /HPC/silica sol/ AlCl_3 (a) film: no H_2S , no heat (b) film: H_2S , no heat (c) film: H_2S , no heat. Suggested peak identification: (1) CuO , (2) CuCl_2 , (3) CuS , (4) CuCl (?).

tated in the film after reaching its solubility limit as observed by a polarized microscope. With increase in HPC (and decrease in silica), the solubility limit of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ increases because the OH groups in HPC provides an electron source for dissolution. Addition of AlCl_3 in HPC and silica also increases the solubility of CuCl_2 (shown in Fig. 1) due to its ionic nature and this is easily dissociated in the solution providing a high CuCl_2 concentration in the homogeneous precursor film. The optimal HPC, silica and AlCl_3 composition (from Fig. 1: point C) is chosen for producing CuS particles from its metal precursors.

C. Particle size characterization

CuS particles produced by the H_2S gas diffusion method are observed by optical, scanning electron and transmission

FIG. 6. XPS deconvoluted $\text{S}(2p)$ spectrum for heated CuS nanoparticles. Suggested peak identification: CuS (1) $\text{S } 2p_{3/2}$, (2) $\text{S } 2p_{1/2}$.

electron microscope. Figures 2(a) and 2(b) are the optical micrographs of CuS particles. With time (no heating), the particles are found to form a chain of network as shown in Fig. 2(b) and this is also indicated by a particle growth [observed in SEM micrograph, Fig. 3(b)]. This network is believed to increase the conductivity of these sulfide films and this can be a potential use in the solar cell applications reported in the literature.¹⁴ The nature of the branching is identified as “fractals.” These fractals follow a diffusion limited colloid aggregation (in three dimensions, $d_f = 2.45$) and the condensation reaction is identified as a monomer-cluster interaction as also predicted by Witten and Sander model.¹⁵ Monomer cluster growth requires a continuous source of monomers which for either chemical or physical reasons, condense preferentially with clusters rather than with each other. It is believed that substantial concentrations of monomers are available from the TEOS derived silicates¹⁶ used in this research.

The SEM micrograph in Fig. 3(a) shows relatively spherical sized particles in the nanometer range. The particles precipitated by H_2S gas exposure were characterized with a Philips TEM. The particle size, distribution, and its structure are illustrated in Figs. 4(a) and 4(b). It is clear from the TEM micrographs that the particles are very spherical in nature and in the range of 2–7 nm. Electron beam diffraction pattern showed the hexagonal symmetry of the CuS particles with a high degree of crystallinity. The isolated CuS particles, as viewed in the TEM, Fig. 4(a), is another indication of the homogeneous distribution of metal precursor in the polymeric matrix. It is to be noted that the particle sizes are in the range of 50–120 nm. Figure 4(b) shows a high-resolution CuS (confirmed by EDS) particle with twins. Twins are a characteristic feature of this hcp structure during early stages of nucleation.¹⁷

D. Surface chemical studies

Besides morphological characterization, it is imperative to facilitate the identification of CuS formation from the reaction between CuCl_2 and H_2S ($\text{CuCl}_2 + \text{H}_2\text{S} = \text{CuS} + 2\text{HCl}$). The XPS binding energies and full width at half maximum

TABLE II. (a) Surface atomic concentrations (calculated from XPS survey spectra) of key matrix elements of CuS nanoparticles as a function of H₂S exposure and heat treatment. (b) Calculated XPS binding energies, Auger energies and the Auger parameter (Al K α radiation, in eV) in selected Cu compounds including CuS nanoparticles.

(a)	Cu	O	Cl	S	Si	Total Cu/Cl	Total Cu/S	Band gap (eV)	
No H ₂ S No heat	1.42	76	0.71	0	22	2	...	2.95	
H ₂ S No heat	4.60	93	0.74	0.53	1.80	6.21	8.7	1.6	
H ₂ S Heat	17.0	79	0.50	1.80	0.89	31.4	9.8	0.9	
(b)	Binding energy E_B (PE)		Kinetic energy E (PE)		Auger energy $E(A)^\alpha$		Auger parameter $E(A)-E(PE)$		$-\Delta\alpha$
	$2p_{3/2}$				$L_3M_{45}M_{45}$				
CuO (C*)	933.6		553.0		918.1		365.1		
Cu ¹⁹	932.4		554.2		918.8		364.6		0.5
Cu ₂ S ¹⁹	932.3		554.3		917.6		363.3		1.8
CuS (C)	931.6		555.0		917.0		362.0		3.1

Note: C—calculated for CuS particles, heat treated, PE=photoelectron, (C*)—calculated for CuO model compound.

(FWHM) of core levels of Cu and S in CuS are listed in Table I (along with C, Cl, and Si binding energies present in the matrix) as a function of H₂S exposure and heat treatment. The C (1s) spectra for all the samples [numbered as: (1) no H₂S, no heat (FWHM 4.5 eV), (2) H₂S, no heat (FWHM 3.7 eV), and (3) H₂S, heat (FWHM 3.6 eV)] listed in Table I exhibit a broad peak consisting of multiple C–H, C–OH (from organic polymer), C–O–C (from HPC) and C=O (surface oxidation) species. It is to be noted that the sample exposed to H₂S gas, followed by heat treatment, shows a decrease in both C–OH and C–O–C content, an indication of the removal of organic sol-gel products during heating.

As expected, the binding energy of the Cu(2p)_{3/2} line (FWHM 2.6 eV) in a non-H₂S exposed sample indicates the presence of both CuO (933.6 eV) and CuCl₂ (934.9), Fig. 5(a). The corresponding Cl (2p) at 199.9 eV represents the Cl[−] in CuCl₂. An additional peak at a lower binding energy ~198.5 eV indicates the presence of AlCl₃ [corresponding Al(2p) at 74.9 eV] in the matrix. The Al(2p) peak structure at 73.8 is that of Al₂O₃ and the polymeric network is probably the mixture of alumina and silica [Si(2p)~102.5 eV] that is responsible for preventing the particle growth. The reduction in the Si(2p) binding energy is due to the insertion of a more ionic Al–O bond thus making the Si–O bond more covalent.¹⁸

After exposing the precursor film to H₂S (sample 2: H₂S, no heat), the Cu(2p)_{3/2} binding energy at 931.6 eV (FWHM 2.3 eV) represents the presence of a divalent Cu in CuS and is consistent with the existing literature.¹⁴ The corresponding S(2p_{3/2}) line at 161.5 eV is an indicative of CuS. An additional small peak at 932.5 eV represents a possible presence of CuCl in the matrix, although its existence is not quite clear. The main Cl(2p) peak at 198.3 eV is mostly due to AlCl₃. When the sample (No. 3) is heated to 150 °C, the binding energy values of Cu(2p) and S(2p) do not vary sig-

nificantly, thus indicating the formation of stable CuS nanoparticles (Fig. 6). In both samples 2 and 3, the main peak at 74.6–74.9 eV indicate the presence of AlCl₃ along with the Si in polymeric silica form (B.E. 102.6 eV).

The relative atomic concentrations of key elements in the CuS nanoparticles matrix for samples 1, 2, and 3 are listed in Table II(a) and the corresponding survey spectra are shown in Fig. 7. Sample 3 shows the highest amount of Cu and S concentration as compared to 1 and 2. These ratios suggest that Cu is in excess and S is relatively deficient in the CuS heated films (suggesting Cu⁺¹ formation). The migrating copper ions fill the copper deficient sites in the top most layer of copper sulfide and improve its stoichiometry.¹⁹ Auger analysis (outer most layer) of the heated CuS sample indicates Cu/S to be 0.9. The Cl concentration decreases and the Cu/Cl ratio increases from samples 1 to 3, indicating the transformation of CuCl₂ to CuS. The reduction of Si and O concentration (from samples 1 to 3) in the film suggests the burning and removal of the sol-gel from the film matrix during heat treatment.

The valence band spectra [Figs. 8(b) and 8(c)] for samples 2 and 3 are quite different from sample 1 [Fig. 8(a)]. A broad feature (4–9 eV) in the valence band spectrum in sample 1 [Fig. 8(c)] indicates the amalgamation of silica (in silica gel) and aluminum (in AlCl₃), but no prominent aluminosilicate network was found in comparison with the studies of various valence band spectra of aluminum silicates.^{18,20} The band gap in sample 3 reduces to 0.9 from 3 eV (in sample 1) with an increase in the Cu(3d) (2.1 eV B.E.) density of states and a similar rise is noted in the Cu concentration in the survey spectrum [Fig. 7(c)]. The reduction in the band gap might lead to an increase in the conductivity of the film, an important parameter to be utilized in possible solar cell applications.

It appears that the change in the binding energy may be

Fig. 7. XPS 0–1200 survey spectra for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{HPC}/\text{silica sol}/\text{AlCl}_3$ (a) no H_2S , no heat, (b) H_2S , no heat, (c) H_2S , heat.

sometimes too small to detect the exact change in the Cu valence state to determine the differences between CuS and Cu_2S . Bhidé *et al.*¹⁴ have shown that metal Auger line intensity ratios such as $\text{Cu}(L_{23}M_{45}M_{45})$ to $\text{Cu}(L_{23}M_{23}M_{23})$ are quite sensitive to the occupancy of valence band states of the metal in their oxides and sulfides. The introduction of a parameter (Auger parameter), defined by the differences between the two line energies (Auger and photoelectron lines) from the same element in the same sample, is attractive because static charge correction is unnecessary. Hence work functions corrections are unnecessary and vacuum level data can be compared to Fermi level data directly. Thus, the concept of the Auger parameter²¹ is useful to determine and confirm the exact chemical state of Cu in the copper sulfide particles in support to the core-level XPS binding energy. This parameter is characteristic of chemical and physical states and is easily measurable to an accuracy of ± 0.1 eV. When the chemical shift in the Auger line is greatly different from that of the photoelectron line, the range in the Auger parameter (α), in eV, can be almost as great as the range in

Fig. 8. Valence band XPS spectra for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{HPC}/\text{silica sol}/\text{AlCl}_3$ (a) no H_2S , no heat, (b) H_2S , no heat, (c) H_2S , heat. (1) $\text{Cu}(3d)$.

the Auger line energy. Table II(b) lists the Auger parameters of the selected Cu compounds of interest. The calculated Cu Auger parameter in sample 3 indicates the presence of Cu^{+2} in CuS , a 1.3 eV shift from that of Cu_2S ,²¹ whereas the core-level binding energy difference is only 0.7 eV. Thus, by monitoring the surface chemistry of Cu and S in nanoparticles, one can be reasonably assured of the formation of CuS films via metal precursors through the gas diffusion method.

IV. CONCLUSIONS

CuS nanoparticles are successfully fabricated from metal precursors through reaction with H_2S gas by the sol-gel process. A hydroxypropyl cellulose derivative is responsible for the production of a uniform particle distribution, while the addition of AlCl_3 increases the Cu solubility limit in the gel matrix. TEM studies of the film show 2–5 nm spherical sized particles in the matrix. XPS studies of the sulfide particles indicate the formation of $\text{CuS}(\text{Cu}^{+2})$. The relative Cu concentration increases with a shift in the valence band leading edge towards the Fermi line indicating the migration of Cu^{+2} ions (increase in $\text{Cu } 3d$ density of states) to the surface during heating, after H_2S exposure, thus improving the stoichiometry of the film. The use of the Auger parameter is suc-

cessfully applied to confirm the presence of divalent Cu⁺² and formation of CuS nanoparticles and not Cu₂S in the H₂S exposed heated film.

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