Synthesis of Polycrystalline Chalcopyrite Semiconductors by Microwave Irradiation

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Polycrystalline samples of the chalcopyrites $CuInS_2$, $CuInSe_2$, and CuInSSe were prepared from stoichiometric mixtures of the pure elements by microwave irradiation. The reactions were performed in sealed quartz tubes in as few as 3 minutes. The products were analyzed by x-ray diffraction, scanning electron microscopy, energy dispersive x-ray analysis, and x-ray photoelectron spectroscopy. The surface morphology and shape of the particles produced by this method suggest that the products are formed from liquid melts. This method could be applied to the production of bulk chalcopyrite as sources for thin film growth.

The chalcopyrites copper indium disulfide ($CuInS_2$) and copper indium diselenide ($CuInSe_2$) are ternary semiconductors with direct band gaps of 1.53 and 1.04 eV, respectively (*1*), which makes them suitable for terrestrial solar cell applications (*2*). Although several methods have been reported for the preparation of these chalcopyrites as thin films (such as evaporation, sputtering, laser ablation, and chemical vapor deposition), many of these require the prior synthesis of bulk material. Traditionally, bulk materials have been prepared by the sintering of the elements (*3*), a process that requires some combination of high temperatures, long reaction times, and specialized apparatus. Recent efforts to develop new syntheses of bulk chalcopyrites have focused on the pyrolysis of single-source organometallic precursors (*4, 5, 6*). As part of our own effort to simplify the synthesis of bulk CuIn dichalcogenides, we found that microwave irradiation of mixtures of the pure elements produces enough heat to complete the reaction to polycrystalline chalcopyrites in as little as 3 min.

Recently, it has been suggested that microwave radiation can be used to increase the rate of selected chemical reactions. For example, the rate of several solution-phase reactions can be accelerated through the high dielectric loss of polar solvents when exposed to microwave energy (*3, 7, 8*); dielectric loss refers to the amount of energy used to align the molecules of a substance with an externally applied electric field, which can result in a large heating effect within a material. Several solvents, such as ethanol, methanol, and water, may be superheated to temperatures 20°C above their normal boiling points by this method. However, it is only recently that solid-state reactions involving metals have been attempted (*9*).

Subjecting continuous metal blocks and films to microwave radiation leads to the generation of electric discharges because large electric field gradients are produced by the metals. In contrast, several investigators have shown that, when exposed to microwave radiation, metal powders may reach temperatures in excess of 1000°C, high enough to allow solid-state reactions to occur. In a finely divided powder, there is a large surface area on each metal particle over which charge may be distributed. As a result, the metal will not discharge but instead will generate heat because of eddy currents created within the powder. As one would expect, metals with high conductivities can be heated to higher temperatures than those with low conductivities. Because the rate of heating is rapid, in some cases as high as 100°C s^{-1}, reactions may be completed in extremely short time periods.

The synthesis of $CuInS_2$ is as follows: Elemental S (0.300 g, 9.38 mmol) was intimately mixed with stoichiometric amounts of Cu and In (0.298 g, 4.69 mmol and 0.538 g, 4.69 mmol, respectively) with a mortar and pestle. All metals used in these experiments were 100 (Se) or 325 (Cu and In) mesh powders; S was purified by sublimation. The mixture was placed in a quartz tube, sealed under vacuum (5×10^{-3} torr), and laid on a firebrick base inside a domestic microwave oven (Sharp Carousel II "Half Pint"). A microwave power of 400 W, at 2450 MHz, was used to irradiate the sample for 1 min, after which the microwave cavity and the reaction tube were hot. The previously reddish mixture had become completely gray. The tube was shaken to redistribute its contents and was then replaced in the microwave oven. The process was repeated twice, for a total of 3 min. After the third time, the quartz tube was removed from the oven and allowed to cool to room temperature before being broken open. The product was a crystalline, bluish-gray powder. Longer reaction times —for example, two cycles of 5 min and one cycle of 15 min—gave products identical in composition and crystallinity to those obtained in the manner described above. The $CuInSe_2$ and the mixed chalcogenide CuInSSe were prepared by similar methods with the appropriate stoichiometries.

During the preparation of $CuInS_2$ and CuInSSe, several blue flashes were observed after 5 to 10 s of irradiation because of the formation of a sulfur plasma in the reaction tube. However, no flashes were observed after this point. This suggests that the reactions producing $CuInS_2$ and CuInSSe occur faster than the rate of sublimation of S into the vapor phase, a diffusion-controlled process. In the case of $CuInSe_2$, no blue plasma was observed; however, the mixture appeared to briefly glow red-hot after about 10 s of irradiation.

The products were uniformly ground for x-ray diffraction (XRD) analysis (*10*). A comparison of the XRD spectra with reported data of known CuIn chalcogenide phases shows that in all cases the chalcopyrite phase is formed as the exclusive crystalline product (*11*) (Table 1). The data show that the products formed by microwave irradiation are identical to those formed by other means. The lack of any extraneous peaks in the diffraction pattern for $CuInS_2$ (Fig. 1) confirms that the intended products are the only crystalline compounds formed. Other

Table 1. Comparison of *d* spacings of CuIn dichalcogenides synthesized by microwave radiation (Expt., experiment) with those reported by Hahn *et al.* (*20*), Cambi and Elli (*12*), and Sui *et al.* (*21*). Where two Miller indices (*hkl*) are given coincidentally, the reflections are not resolved within the resolution of the experiment.

hkl	*d* spacing (Å)					
	$CuInS_2$		CuInSSe		$CuInSe_2$	
	Expt.	(*20*)	Expt.	(*12*)	Expt.	(*21*)
112	3.19	3.20	3.29	3.27	3.33	3.35
211	2.41	2.41	2.47	2.47	2.51	2.53
213	2.06	2.06			2.15	2.15
204/220	1.96	1.96	2.01	2.01	2.04	2.04
116/312	1.68	1.68	1.71	1.71	1.74	1.74
400/008			1.42	1.41	1.45	1.45
316/332	1.27	1.27	1.30	1.30	1.33	1.33

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possible products with stoichiometries other than 1:1:2 (Cu:In:chalcogen) are not formed as crystalline materials. In addition, the formation of CuInSSe (*12*) is not accompanied by that of either $CuInS_2$ or $CuInSe_2$, even for short reaction times.

Our x-ray photoelectron spectral (XPS) analysis (*13*) of the products indicates that the constituents are not present in their elemental forms. The spectral shifts are consistent with previously reported values for the bulk products (*14*, *15*); the carbon and oxygen peaks observed are caused by adventitious hydrocarbons adsorbed on the surface.

The morphology of the as-synthesized products was investigated by scanning electron microscopy (SEM) (*16*). A number of distinct particle shapes are formed (Fig. 2A); of particular note are the spheres (Fig. 2B) seen in the upper right and lower left of Fig. 2A. Such spherical particles would be expected if crystal growth occurred as a result of homogeneous nucleation in a liquid melt, followed by rapid quenching. The surface of a nonspherical particle is covered by domed growths (Fig. 2C). This latter morphology is undoubtedly also a result of homogeneous nucleation during the reaction. Rapid quenching after the microwave irradiation is expected to produce amorphous material, which is indeed observed (Fig. 2, B and C). Furthermore, a variation in the Cu:In:chalcogen ratio is found by energy dispersive x-ray (EDX) analysis (*17*). Because only the chalcopyrite phase is observed by XRD, the nonstoichiometric elemental composition must be attributable to the presence of amorphous $(Cu_2S)_x(In_2S_3)_{1-x}$.

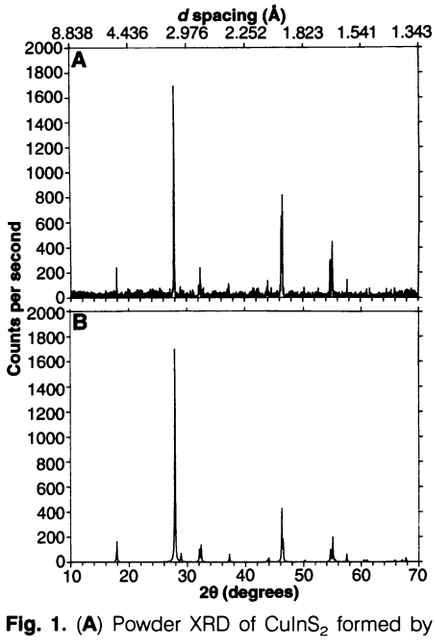

Fig. 1. (**A**) Powder XRD of $CuInS_2$ formed by microwave irradiation, and for comparison, (**B**) a computer-generated spectrum based on *d* spacings reported previously (*11*).

Because there are a myriad of possible pathways by which the Cu, In, and chalcogen can combine, we performed several additional experiments to determine the mechanism of chalcopyrite formation. For example, we found that although Cu and S react to produce copper sulfide (Cu_2S or CuS, depending on reagent stoichiometry), reacting In and S does not give the corresponding In product (In_2S_3). This shows that the dielectric loss of Cu is high enough to create sufficient heat to initiate the reaction, whereas the dielectric loss of In is not. An alternative explanation for the lack of reactivity between In metal and S may be the high surface tension of the In, which reduces the rate of reaction. However, we feel that the large difference in the conductivities of the two metals (Cu = 0.652 mho/m, In = 0.119 mho/m) (*18*) provides a better explanation for differences in reactivity.

Because the temperatures reached are certainly high enough to melt In (melting point, 157°C), one might envisage a multistep process in which the Cu heats up and melts the In, possibly through the formation of a CuIn alloy. It has recently been shown that CuIn alloy reacts with S to give $CuInS_2$ (*19*). However, microwave irradiation of a stoichiometric mixture of Cu and In, in the absence of S, does not yield the CuIn alloy. Instead, under reaction conditions identical to those described above, no reaction was observed as indicated by XRD. The Cu and In had segregated, suggesting that the In had melted but no dissolution of the Cu had occurred. From these observations, we propose that the formation of CuIn dichalcogenides occurs as follows: microwave irradiation causes Cu to react with the chalcogen to form Cu chalcogenide. Either the exothermic formation of the Cu chalcogenide or the heating of the Cu causes the In to melt. Dissolution of the Cu chalcogenide and the remaining chalcogen in the molten In produces a homogeneous liquid melt from which the chalcopyrite crystallizes (Eq. 1) (E = S, Se)

$$CuE(soln) + In(l) + E(soln) \rightarrow CuInE_2(s) \quad (1)$$

This proposal is consistent with the morphology of the chalcopyrite product. Supporting evidence for this mechanism is given by the observation that copper sulfide reacts with In and a stoichiometric equivalent of S to give $CuInS_2$, which is identical to samples prepared from the three elements.

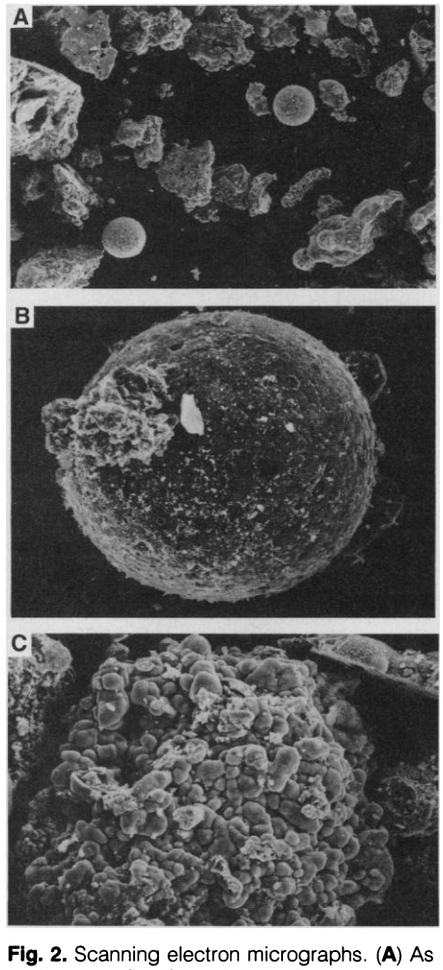

Fig. 2. Scanning electron micrographs. (**A**) As synthesized $CuInS_2$ particles. (**B**) Higher magnification view of one such particle. (**C**) The surface of a nonspherical particle.

Bulk CuIn dichalcogenides are readily prepared from their constituent elements with a simple and inexpensive microwave oven. Although the products described herein are not of semiconductor quality and this methodology is not applicable to all elements (for example, liquid mercury is unsuitable), we believe that a wide range of ternary and quaternary chalcogenide compounds may be prepared by microwave irradiation.

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Proliferation of Human Smooth Muscle Cells Promoted by Lipoprotein(a)

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Elevated blood concentrations of lipoprotein(a) [Lp(a)] and its constituent, apolipoprotein(a) [apo(a)], constitute a major risk factor for atherosclerosis, but their physiological activities remain obscure. Lp(a) and purified apo(a) stimulated the growth of human smooth muscle cells in culture. This effect resulted from inhibition of plasminogen activation, and consequently the activation by plasmin of latent transforming growth factor–β, which is an inhibitor of smooth muscle cell growth. Because smooth muscle proliferation is one of the hallmarks of atherosclerotic lesions, these results point to a plausible mechanism for the atherogenic activity of Lp(a).

A high concentration of Lp(a) in blood constitutes a major risk factor for atherosclerosis, coronary heart disease, and stroke (*1*). Lp(a) differs from low density lipoprotein (LDL) by the presence of the glycoprotein apo(a). Because the amino acid sequence of apo(a) is approximately 80% identical to that of plasminogen (*2*), it is possible that the pathophysiology of Lp(a), including effects on fibrinolysis, is attributable to apo(a). Lp(a) binds to endothelial and macrophage cells and to extracellular components such as fibrin and inhibits cell-associated plasminogen activation (*3, 4*). To date, no direct effect on cell proliferation has been demonstrated. Abnormal proliferation and migration of vascular smooth muscle cells is a major component of vascular disease, including atherosclerosis and restenosis after angioplasty. Elevated plasma Lp(a) concentration is one of the most important risk factors for both of these conditions (*1, 5*).

To investigate the effects of Lp(a) on smooth muscle cells, we subjected cultured human and rat smooth muscle cells to plasma-derived Lp(a) and to its constituent parts, LDL and apo(a). Human aortic vascular smooth muscle cells (VSMCs) derived from healthy donor tissue were cultured in Dulbecco's modified essential medium (DMEM) plus 10% fetal calf serum (FCS) as described (*6*). Addition of Lp(a) to subconfluent human VSMCs stimulated their proliferation in a dose-dependent manner (Fig. 1A). Apo(a) had a similar effect, although a higher concentration was required for half-maximal stimulation. This disparity could be due to conformational differences between free apo(a) and its lipoprotein-associated form, Lp(a), or to size variants of apo(a) that differ in the number of repeated kringle domains. The recombinant apo(a) is a smaller isoform [relative molecular mass (M_r) ~ 500,000] than those present in the donor's plasma (M_r ~ 650,000 and 800,000). Addition of 500 nM Lp(a) to human VSMCs caused a reduction of the time taken for cells to double in number from 82 ± 4 hours to 47 ± 4 hours (Fig. 1B). LDL had no effect on cell proliferation at all concentrations tested, up to 1 μM. In contrast to the effect seen on human cells, neither Lp(a), apo(a), nor LDL affected the proliferation of cultured rat VSMCs (Fig. 1C).

Further studies were performed to elucidate the nature of the stimulation of proliferation by Lp(a) and apo(a). It is possible that apo(a) could act as a mitogen because it shares global homology and 38% amino acid identity with hepatocyte growth factor, which is a mitogen for hepatocytes and several other cell types (*7*). Alternatively, apo(a) could act by competitive inhibition of surface-associated plasminogen activation and the subsequent activation of transforming growth factor–β (TGF-β) by plasmin. The TGF-β family consists of a number of related cytokines of diverse function. TGF-β is a potent inhibitor of cell proliferation for a number of anchorage-dependent cells, including smooth muscle cells, and may be a physiological modulator of smooth muscle cell proliferation during wound healing and atherosclerosis (*8*). Latent TGF-β is a homodimer in which the active moiety is noncovalently linked to the NH_2-terminal portions of the propeptide (*9*). Although activation of TGF-β may be achieved in vitro by acid treatment, plasmin can activate the latent molecule by cleavage within the propeptide region and is a likely candidate for a physiological regulator of TGF-β activity (*10*). Owing to the antiproliferative effect of TGF-β on smooth muscle cells, we hypothesized that apo(a) could act on cultured human VSMCs by interfering with the activation of latent TGF-β. Such an effect might not be expected for rat cells because they synthesize little TGF-β in culture (Table 1), whereas addition of active TGF-β to rat VSMCs suppresses their proliferation (Fig. 1C). Thus, Lp(a) could act in a species-specific manner on cultured human VSMCs by interfering with the activation of plasminogen and, therefore, TGF-β.

Plasmin activity associated with the cells was reduced sevenfold by Lp(a) and fivefold by apo(a) in both human and rat VSMC cultures (Fig. 2A). The plasmin activity in the conditioned medium was also reduced by the Lp(a) and apo(a) by almost twofold, but was much lower than cell-associated plasmin activity in both VSMC cultures (Fig. 2B). This is consistent with previous findings that Lp(a) is a more potent inhibitor of surface-associated, rather than fluid phase, plasminogen activation (*3*).

To exclude the possibility that Lp(a) was affecting the synthesis of plasminogen activators (PAs), we measured PA levels in the human cell cultures in the absence and

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