

Doping of CuInSe₂ Crystals: Evidence for Influence of Thermal Defects

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Annealing of p-CuInSe₂ crystals at low (250–300 °C) and high (600–650 °C) temperatures in the presence of CuInSe₂ powder with a variety of (native) dopants showed the temperature rather than the nature of the dopant to be the major factor in determining the resultant carrier type and concentration. Experiments without added dopant indicate, for samples from a different boule, that type conversion occurs upon annealing between 550 and 650 °C. These results can be explained by thermally induced changes in relative concentrations of intrinsic defects (that were frozen in during crystal cooling) via complex formation and temperature-dependent ionization of defects and their complexes.

Introduction

Control over the electrical properties of CuInSe₂ is complicated by the possible presence of a variety of intrinsic, electrically active defects and resulting high compensation ratios. Even such a basic procedure as doping, without external dopants, becomes problematic because of the large number of possible defect equilibria. In addition, as pointed out by Binsma for CuInS₂,¹ annealing in the presence of only one component does not correspond to equilibrium conditions for a ternary compound. This complicates straightforward interpretation of thermal doping experiments in vacuo or those with only Cu, In, or Se added.

In the course of attempts to prepare high-resistivity samples of CuInSe₂, for studies of the semionic character of this mixed conductor² we performed several series of doping experiments. The results point to the thermal history of the samples as an important and at times decisive factor for determining the electronic properties after thermal doping.

Experimental Section

Crystals for samples 1–5 were obtained via the Solar Energy Research Institute (Golden, CO, from K. J. Bachmann and M. Fearheiley; cf. ref 3). They were grown by directional solidification of nearly stoichiometric melts under 10³ Pa of Se pressure. The initial electrical properties of the 20 samples cut from these crystals showed considerable scatter (cf. Figures 1–5). Their specific resistivities ranged from 3 to 190 Ω cm (average 45; standard deviation 45), their hole mobilities from 5 to 30 cm²/(V s) (average 16; standard deviation 17), and their net hole concentration from 3.5 × 10¹⁵ to 180 × 10¹⁵ cm⁻³ (average 30; standard deviation 50). Crystals for samples 24–27 were obtained via the Institute for Physical Electronics, University of Stuttgart (from Haupt and Hess, cf. ref 4). They were grown by the vertical Bridgman method, by cooling the prereacted melt from 1020 °C at 2 °C/h until 750 °C was reached and from there at 10 °C/h. As can be seen from the data marked initial in Tables I–III, the 14 samples cut from the boule prepared in this way showed less scatter in their electrical properties than did samples 1–5. Their specific resistivities ranged from 0.3 to 6.4 Ω cm (average 1.6; standard deviation 1.4), hole mobilities from 5 to 31 cm²/(V s) (average 18; standard deviation 6), and net hole concentrations from 1.6 × 10¹⁷ to 9.7 × 10¹⁷ cm⁻³ (average 3.3; standard deviation 2.1). Square or rectangular plates with minimal areas of 2 × 2 mm² and ca. 1 mm thick were cut from the boules with a wiresaw and hand polished with 5-μm Al₂O₃ in H₂O. Finer polish did not yield improved (more reproducible) results, as measured by electrical resistivity. The samples were then placed, with the polished side

upward, on a holder suitable for electrical resistivity and Hall effect measurements by the van der Pauw method.⁵ The samples were held in the holder by beeswax. Ohmic contacts were made on the edges of the polished surface, with dots of Ga–In alloy, which were found to give the most reproducible results even on p-type samples. For the Hall effect measurements a field of 20 kG and currents of 0.15–1.1 mA (depending on the sample's resistivity) were used. WDS and EDS microprobe analyses showed all samples to be slightly Cu deficient, with $x = 0.47$ – 0.5 in (CuSe₂)_x(In₂Se₃)_{1-x}, and to be between 0.5 and 1 at. % Se deficient.

For doping and thermal annealing experiments the samples were placed in 10–25-mL quartz ampules, previously cleaned with aqua regia to remove inorganic impurities, H₂O rinsed, washed with 10% detergent in H₂O solution to remove organic impurities, rinsed several times with distilled water, and dried overnight at 140 °C. To mimic equilibrium conditions for all treatments, except anneals in vacuo, 25–100 mg of finely powdered CuInSe₂ (p-type, net $N_a \sim 10^{17}$ cm⁻³) were added to avoid uncontrolled decomposition of the samples. Se and In₂Se₃ were added as powders (25 and 40–90 mg, respectively). In was added as high-purity wire (25–50 mg), and Cu was sputtered directly onto the samples, yielding 10–15-nm-thick films. Loaded ampules were evacuated to a pressure of less than 1.3 × 10⁻³ Pa (10⁻⁵ Torr). To avoid contamination, a system of two ampules connected via a "T" with a glass frit to a vacuum system was used. The sample plus additives was put into the extra ampule. After a stable pressure was obtained, the second ampule was flame treated, filled (by turning the "T" with the sample plus additives), and sealed.

For the first series (with added dopants or in vacuo) each ampule contained one sample. The ampules were placed horizontally in a box furnace, four at a time. The oven was switched on for 75 min in the case of low-temperature (LT) doping and 90 min for high-temperature (HT) doping. Final temperatures were reached within 3–7 min. The oven was then switched off, and the samples were allowed to cool for 0.5 (LT) or 1 h (HT) to 50–100 °C. All samples used for doping experiments were subjected to two sequential treatments with a complete polishing treatment (including thorough removal of contacts) in between: 1A–D, Se-vacuum; 2A–D, In–In; 3A–D, In₂Se₃–Cu; 4A–D, Cu–In₂Se₃; 5A–D, vacuum–Se. The first treatment was at low oven temperature (250 °C for samples A, B; 300 °C for C, D), and the second one at higher temperature (600 °C for A, B; 650 °C for C, D). Thus crystals first LT heated with Cu were HT heated

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(3) Bachmann, K. J.; Fearheiley, M.; Shing, T. H.; Tran, N. *Appl. Phys. Lett.* **1984**, *44*, 407. Fearheiley, M. *Sol. Cells* **1986**, *16*, 91.

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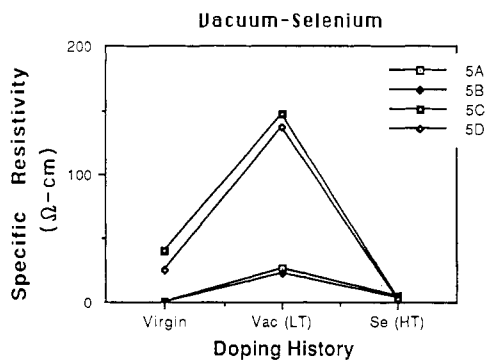


Figure 1. Effect of doping treatments on specific resistivity (in Ω cm) of CuInSe_2 crystals. Missing point(s) indicate sample(s) that were (and often could) not be measured. The samples were first LT annealed in vacuo and then HT annealed with Se. For samples A,B: LT = 250 °C, HT = 600 °C. For samples C,D: LT = 300 °C, HT = 650 °C.

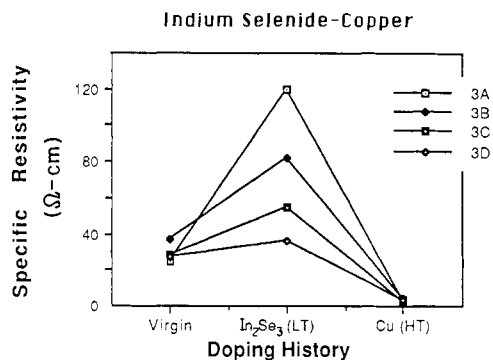


Figure 2. As Figure 1 with LT In_2Se_3 and HT Cu anneal.

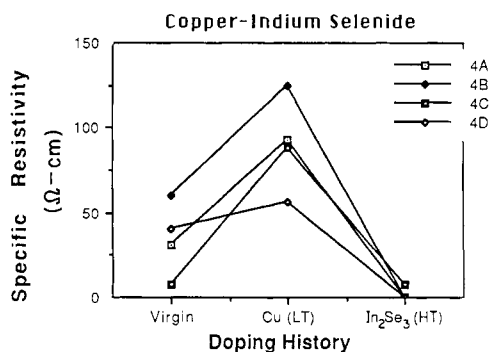


Figure 3. As Figure 1 with LT Cu and HT In_2Se_3 anneal.

with In_2Se_3 and vice versa. LT Se heating was followed by HT vacuum anneal and vice versa. In this way we tried to reverse changes, brought about by the first doping treatment. Only the In heating was done at both LT and HT.

For anneals without added dopant, each ampule contained two samples, A and B or C and D. As a further precaution against possible artifacts, the ampules were placed in stainless steel or Ni cylinders to avoid temperature gradients, in the same box furnace used previously. Annealing temperatures were kept below that reported for the chalcopyrite-sphalerite transition (810 °C), viz., between 450 and 750 °C, reached from 200 °C at a controlled rate of 300 °C/h. The samples were kept at their annealing temperature for 24 h, after which they were quenched by dropping the ampules in cold water. Before performing electrical measurements, the samples were repolished.

Results

Figures 1-5 summarize the results from the doping experiments on CuInSe_2 . The use of Cu, In, or Se as potential dopants is obvious. In_2Se_3 , which should decompose into In_2Se and Se_2 , was used in an attempt to decrease relative Cu content. Vacuum anneal was meant to decrease

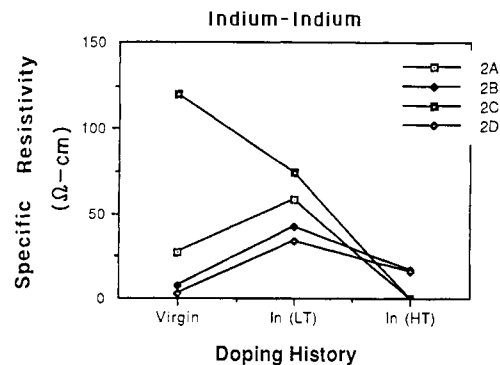


Figure 4. As Figure 1 with LT In and HT In anneal.

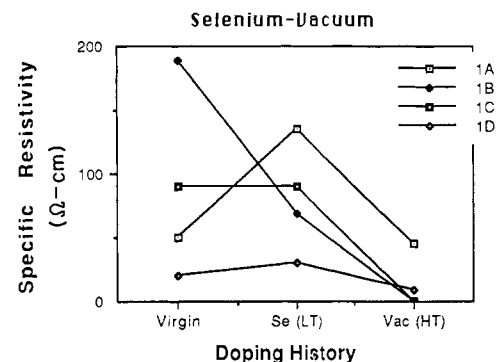


Figure 5. As Figure 1 with LT Se and HT vacuum anneal.

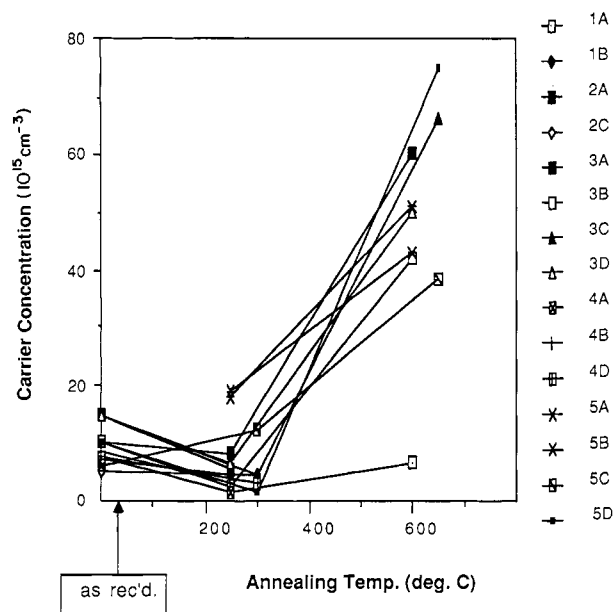


Figure 6. Effect of annealing temperature on carrier concentration for most of the samples of Figures 1-5. The initial, "as received" condition is set arbitrarily at 25 °C. The following points (carrier concentration in 10^{15} cm^{-3} in parentheses) are not included in the plot: 1A, initial (5); 1C, initial-300-650 °C (3.6-13-63 n-type); 1D, initial-300-650 °C (9.6-27-34); 2B, initial-250-600 °C (180-17-46); 2C, 650 °C (150, n-type); 2D, initial-300 °C (120-9); 4C, initial-300-650 °C (95-3.7-22). All other missing points could not be measured reproducibly.

Se content, due to the relatively high vapor pressure of Se.

Only in two cases, one with LT In and HT In anneal (sample 2C) and one with LT Se and HT vacuum anneal (sample 1C), was type conversion to n-type obtained, after the HT anneal. These samples also had the lowest initial net hole concentrations (3.5×10^{15} and $5 \times 10^{15} \text{ cm}^{-3}$). Their companion samples 2D and 1D, which were subjected to the same annealing procedures but had 20 and

Table I. Electrical Properties of Samples 24 before and after Thermal Doping

sample	temp quenched from, ^a °C	ρ , Ω cm	μ , cm ² /(V s)	p/n, 10 ¹⁷ cm ⁻³	type
24A	initial	1.0	18	3.3	p
	750	0.3	170	1.2	n
	550	5.2	13	0.9	p
	650	0.2	280	1.4	n
24B	initial	1.0	17	3.5	p
	750	0.2	180	1.7	n
	550	6.0	12	0.9	p
	650	0.2	145	2.7	n
24C	initial	0.8	20	4.8	p
	650	0.1	285	3.2	n
	450	0.8	225	0.3	n
24D	initial	1.0	22	2.9	p
	650	0.1	240	3.8	n
	450	0.8	205	0.4	n

^aThe order of the temperatures gives the sequence in which the annealing experiments were done, with a room-temperature cool-measure-repolish cycle before each experiment.

Table II. Electrical Properties of Samples 25 before and after Thermal Doping

sample	temp quenched from, ^a °C	ρ , Ω cm	μ , cm ² /(V s)	p/n, 10 ¹⁷ cm ⁻³	type
25A	initial	1.5	12	4.0	p
	550	1.2	185	0.3	n
	650	23	6	0.5	p
25B	initial	1.9	14	2.6	p
	550	1.4	130	0.3	n
	650	21	6	0.4	p
25C	initial	1.9	14	2.4	p
	450	0.6	12	9.0	p
	650	0.2	13	26	p
25D	initial	6.4	29	3.5	p
	450	1.1	29	2.0	p
	650	0.2	35	12	p

^aThe order of the temperatures gives the sequence in which the annealing experiments were done, with a room-temperature cool-measure-repolish cycle before each experiment.

3 times higher initial net hole concentrations, were not type converted. Considerable scatter exists in the data, but with the exceptions of samples 1A,B (LT Se, HT vacuum anneals) and 1C,D and 2C,D (see above) reasonable to very good reproducibility was found for samples subjected to the same treatment sequence (in different ampules). This suggests that the cleaning and sealing procedures did not, in most cases, introduce uncontrolled factors.

Figures 6 and 7 show the effect of heating on carrier concentration as determined by Hall measurements (see Discussion).

Tables I–III give the results of the thermal annealing experiments in which no dopant was added. As the results for samples 24 suggested the existence of a definite temperature range for type conversion between 550 and 750 °C, samples 25 were annealed at lower temperatures. Results on those samples led to experiments on samples 26 and 27 to determine to what extent the idea of one range of temperature for type conversion holds. For a given pair of samples reproducibility was good, with the exception of samples 25C,D. For the last sample and for 26D, exceptionally high hole mobilities were measured. However, our discussion will be based mostly on trends, rather than on absolute numbers.

Discussion

Review of the Literature. A short summary of CuInSe₂ doping has been given recently by Tomlinson.⁶

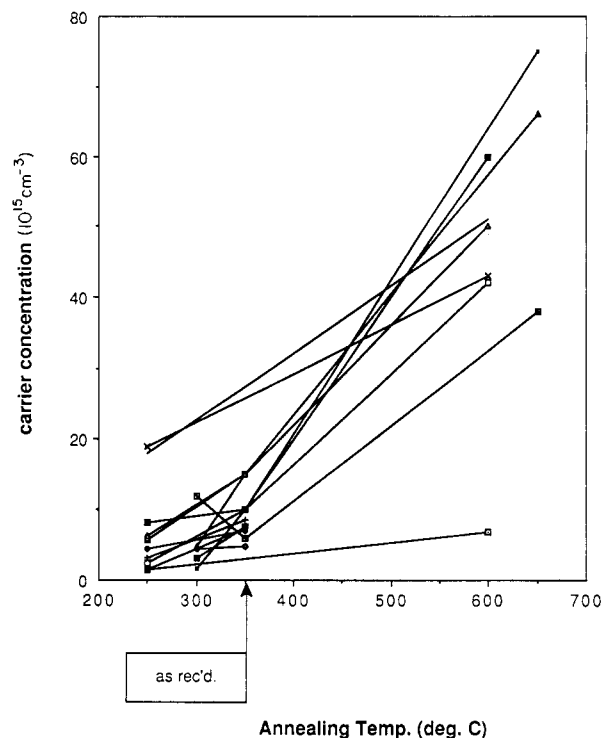


Figure 7. As Figure 6 with the initial, “as received” condition chosen at 350 °C.

Table III. Electrical Properties of Samples 26 and 27 before and after Thermal Doping

sample	temp quenched from, ^a °C	ρ , Ω cm	μ , cm ² /(V s)	p/n, 10 ¹⁷ cm ⁻³	type
26A	initial	2.1	16	2.0	p
	550	2.4	12	2.3	p
26B	initial	2.1	16	2.0	p
	550	3.0	11	1.9	p
26C	initial	0.3	18	1.6	p
	450	0.5	14	9.4	p
	650	0.2	20	12.5	p
26D	initial	0.3	31	6.1	p
	450	0.5	18	7.0	p
	650	0.2	24	13	p
27A	initial	1.1	17	3.4	p
	550	1.8	17	2.1	p
	650	0.5	86	1.4	n
27B	initial	1.3	5	9.7	p
	550	3.2	11	1.8	p
	650	0.3	66	3.0	n

^aThe order of the temperatures gives the sequence in which the annealing experiments were done, with a room-temperature cool-measure-repolish cycle before each experiment.

A direct comparison between results reported in the literature is complicated as annealing conditions vary and the description of experimental procedures is not always complete. One fact that is uncontested, however, is that high Se pressure dopes CuInSe₂ samples p-type at elevated temperatures. Parkes et al.⁷ found that a 15-min anneal at 600 °C under an excess of Se pressure ($>3 \times 10^4$ Pa) was sufficient to type convert an n-type sample to p-type. Masse et al.⁸ annealed CuInSe₂ crystals obtained by 3 °C/h cooling from the melt in an atmosphere with excess Se (an exact value for the Se pressure was not given) for various

(6) Tomlinson, R. D. *Sol. Cells*. 1986, 16, 17.

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durations (minutes to days) at 300–750 °C. They found increasing (p-) resistivity and decreasing hole concentration with increasingly stronger conditions. Bachmann et al.³ found that a 4-h anneal at 900 °C of n-type CuInSe₂ resulted in low-resistivity p-type samples, when performed at 10⁴ Pa of Se pressure. Another sample annealed under the same conditions but at 10³ Pa of Se pressure had nearly 100 times higher resistivity and a corresponding lower net carrier concentration. It therefore follows that Se is also capable of subliming from the crystal, causing it to become more n-type. For this reason CuInSe₂ powder should be added to ampules to prevent sample decomposition. Experiments performed without such a precaution are difficult to interpret.

Shih et al.⁹ annealed p-CuInSe₂ samples, grown from the melt and cooled at 10 °C/h from 810 °C, in vacuo at various temperatures and for various durations. They found that crystals heated in vacuo (with CuInSe₂ powder added; cf. ref 10) at 160 °C for increasing time intervals exhibited increased resistivity until a plateau was reached for anneals for 40 min or longer. Samples heated in evacuated ampules for 8 min each at increasing temperatures exhibited increased resistivity up to 300 °C. Those crystals annealed at higher temperatures were type converted and had a specific resistivity that decreased as a function of the doping temperature. This phenomenon was ascribed to Se out-diffusion (and in-diffusion of Se vacancies). Indeed, von Bardeleben, in a careful study of Se self-diffusion in CuInSe₂,¹¹ showed that Se_i can diffuse at 700 °C. However, such diffusion is expected to be negligible due to steric and energetic effects, at the temperatures where type conversion was observed (200–400 °C). Possibly Se sublimed from the surface of the crystal, thereby causing an excess of In and Cu atoms, which could in-diffuse, converting the material to n-type.

Numerous examples exist of Cu or In contacts being used for junction formation or type conversion at moderate temperatures (cf. ref 6 and 8). Samples with such contacts, heated at 200–300 °C under argon for 10 min or longer will display rectifying behavior. Abrasive lapping followed by selective chemical etching was used by Tell et al.¹² to determine an interdiffusion coefficient for Cu in p-type CuInSe₂ at 200 and 300 °C (5.5×10^{-10} and 1.8×10^{-8} cm²/s, respectively). They concluded that since the same result was obtained for Cd and Zn, some (intrinsic) mobile species was diffusing out of the sample, possibly Se.

On the basis of crystal chemical considerations¹³ and the estimated formation enthalpy of Se_i in CuInSe₂,¹⁴ the mobility of Se in CuInSe₂ is expected to be considerably smaller than that of Cu or In. It is therefore unlikely that n-doping at these temperatures was caused by Se out-diffusion from the bulk. Experiments by us utilizing the technique of electron-beam-induced current to examine Cu and In thermal diffusion have yielded different diffusion coefficients for the two species, suggesting that they do not act so much as a sink for species out-diffusing from the crystal, but they themselves enter the sample.¹⁵

Analysis of Doping Experiments (Samples 1–5). Only in two instances was type conversion obtained. An-

nealing at high temperatures under Se vapor yielded nearly the same electronic properties as the high-temperature Cu treatments. Low-temperature doping generally resulted in increased resistivity, whereas high-temperature treatments caused a significant reduction in resistivity. The net carrier concentration decreased after the low-temperature treatments and then increased after the higher temperature anneals, while mobility usually increased after each treatment, *regardless of the dopant and the temperature*. Thus we attribute the broad trends that are observed as being due to changes within the samples themselves, that occurred at the temperatures of the doping treatments, regardless of the dopant atmosphere. The reason for this can be that during the original crystal growth a particular acceptor goes into the solid solution at higher temperatures, thereby increasing the p-character of the sample. As the crystal rapidly cooled, this defect would be unable to precipitate out of solid solution and would become frozen into the sample, resulting in an increased carrier concentration. A subsequent lower temperature anneal would allow this defect to precipitate out of the solid solution, resulting in a lower carrier concentration. In this way each thermal treatment would induce carrier concentrations in the sample corresponding to the temperature of the anneal and the thermal history of the sample.

Thermal Doping. The results given in Tables I–III suggest that such a process might indeed occur in CuInSe₂. Such thermal defects (formed by heating and quenching) in elemental and binary semiconductors have been reviewed by Mashovets.¹⁶ As possible causes for changes in the electronic properties of semiconductors upon heating and quenching he gives the following: intrinsic defect formation, including complexes (e.g., thermally activated formation of Frenkel pairs or V_{Cu}–In_{Cu} complex formation); interaction between intrinsic and extrinsic defects (Fe_{In} is a possible extrinsic defect in CuInSe₂); precipitation of impurities from solid solution (as a result of the temperature dependence of impurity solubility); diffusion of intrinsic and/or extrinsic defects to or from the surface. In the case of binaries deviations from stoichiometry present another complicating factor, which is even more valid for a ternary such as CuInSe₂, with a known range of existence especially toward the indium-rich side of the Cu₂Se–In₂Se₃ pseudobinary.^{3,17}

Except for the earlier mentioned work of Shih et al.^{9,10} no correlation between annealing temperature and electronic properties has been reported for CuInSe₂. Experiments on p-CuInS₂ (grown by chemical vapor transport) showed a sharp increase in resistivity after 20-min vacuum anneals above ca. 300 °C, both with and without the addition of CuInS₂ powder.¹⁸ This result was attributed to loss of sulfur or to thermal defect creation. In a subsequent study by the same group the possibility of formation of donor-acceptor complexes during crystal growth and their ionization at high temperature was suggested.¹⁹

More data are available for group III–group V compounds such as GaAs and InAs. For InAs p–n conversion has been reported after 400 °C anneal and quenching and restoration to the preanneal properties by a subsequent low-temperature heat treatment. Also for InSb, n–p conversion upon annealing has been found. In both cases changes in the solubility of extrinsic defects were suggested

(9) Shih, I.; Champness, C. H.; Vahid Shahidi, A. *Sol. Cells* **1986**, *16*, 27.

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(14) Neumann, H. In *Verbindungshalbleiter*; Unger, K., Schneider, H., Eds.; Geest & Portig: Leipzig, 1986; Chapter 9, and quoted in ref 2b.

(15) Solz, D.; Dagan, G.; Cahen, D. *Solid State Ionics* **1988**, *28–30*, 1105.

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(17) Folmer, J. C. W.; Turner, J. A.; Noufi, R.; Cahen, D. *J. Electrochem. Soc.* **1985**, *132*, 1319.

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(19) Ueng, H. Y.; Hwang, H. L. *J. Appl. Phys.* **1987**, *62*, 434.

as the cause for the type conversion. Also 850 °C anneal and subsequent quench of n-InAs was found to decrease the carrier concentration, a result that was explained by the formation of thermally induced, electrically inactive defect complexes.¹⁶

For n-GaAs Wang,²⁰ Ikoma,²¹ and Khokhlov et al.²² found carrier concentrations that increased with increasing temperature above 250 °C. Hurle²³ suggested that this was caused by the formation of arsenic vacancies, due to a shift toward the Ga-rich side of the single-phase field at the higher temperature. Unfortunately the phase diagram for CuInSe₂ is quite incomplete in the temperature domain of the doping experiments performed here, so it cannot be used to confirm this hypothesis. Look et al.²⁴ observed reversible changes between (n-) semiconducting and semi-insulating behavior for GaAs, upon 5-h vacuum anneal at 950 °C and quenching (semiinsulating) or slow, oven cooling (semiconducting). They explained their results in terms of the high-temperature formation of two intrinsic defect complexes, one a donor and the other, which is unstable toward slow cooling, an acceptor.

Figures 6 and 7 show an increasing net carrier concentration as a function of annealing temperature, in most of the doping experiments. The low- and high-temperature anneals generally fit this model. However, the thermal history of the crystals before they were used in these experiments is not well-known (contrary to what was the case for samples 24–27). In Figures 6 and 7 the “as-received” condition of the samples is chosen as 25 and 350 °C, respectively. As is apparent from inspection of the graphs, the fit is better with the latter choice, where mostly a monotonic increase in net carrier concentration with increasing annealing temperature is obtained. As it is likely that the source boule was rapidly cooled from ca. 800 °C to room temperature, one would expect the resulting net carrier concentration to be much higher (reflecting an annealing temperature of 800 °C). However, the time during which the samples were stored (a period of several years) could have allowed annealing of the defects to occur at room temperature, leading to a defect concentration level equal to that of an anneal at 350 °C by the time these experiments were performed (cf. GaAs in ref 25).

Let us now consider the results from the thermal annealing experiments (i.e., without added dopants), given in Tables I–III. Annealing at 450 °C consistently failed to type-convert the samples (24C,D; 25C,D; 26C,D). A modest mobility increase is seen for samples 25 and 26 together with an increased net acceptor concentration. In sample 24 a drastic decrease in net donor concentration is coupled with only small decreases in mobility. The mobility, μ , is influenced by ionized impurities, according to

$$\mu \sim (m^*)^{1/2} N_i^{-1} T^{3/2}$$

where m^* is the effective mass of the majority carrier, T is the absolute temperature, and N_i is the concentration of ionized impurities. The results then suggest that annealing at 450 °C also after prior 650 °C anneal leads to an increase in total acceptor concentration, coupled with

a (smaller) decrease in total donor concentration. The results for 750 °C anneals indicate that at that temperature the opposite processes occur (samples 24A,B).

Results for 550 and 650 °C anneals are less straightforward as can be seen from comparison between the opposite results for samples 25A,B and 27A,B. Anneals at 650 °C of untreated samples and of those first heated at 750 and 550 °C (24A,B) or 550 °C only (27A,B) can be explained by a decrease in total acceptor concentration. But, as noted above, results for 25A,B (after 550 °C anneal) are opposite. Except for samples 26A,B, all results for 550 °C anneal can be interpreted as a decrease in acceptor concentration coupled with some increase in donor concentration. In the case of samples 26A,B, 550 °C anneal had little effect.

It appears thus that for these samples annealing above 550 °C mostly leads to decreases in acceptor concentration with some decrease in donor concentration, while 450 °C anneals have the opposite effect. This must be the reason for the existence of a critical temperature range for type conversion around 550 °C. We note that Shahidi et al. found similar behavior for their samples,¹⁰ but in the 250–350 °C range. To explain our results, we note that both with and without type conversion the changes in net carrier concentration are relatively small. This indicates that there exist large “background” concentrations of ionized donors and acceptors, i.e., the samples are strongly compensated. Thus small changes in the population of one type of defect can lead to type conversion. Our results can be rationalized by assuming the following: (1) Initially high concentrations of single defects were frozen in during crystal growth. Schottky defects, which need grain boundaries or dislocations to form (and be annihilated), and metal anti-site defects (if the quenching temperature is close to the sphalerite–chalcopyrite transition) are likely candidates. On the basis of analyses of photoluminescence data (to be published) and the experimentally determined stoichiometries we expect Cu_{In}, In_{Cu}, V_{Se}, V_{Cu}, and V_{In} to be the dominant defects that are frozen in. (2) Upon annealing, some of these defects associate. At higher temperatures dissociation of some of the associates becomes possible.

Low-temperature anneal effects can then result from defect association of the types V_{In}–In_{Cu} (\rightarrow V_{Cu}), V_{Cu}–Cu_{In} (\rightarrow V_{In}), and V_{Se}–V_{In}. High-temperature anneal effects can be caused by dissociation of these pairs and/or formation of associates of the type V_{Se}–V_{Cu}. These hypotheses illustrate the complexity of the doping mechanisms and the importance of thermal defects for control over the electronic properties of CuInSe₂.

Conclusions

We have presented results that suggest strongly that thermal defects can play a decisive role in determining the electrical characteristics of CuInSe₂ crystals. Their effect is probably enhanced by the high compensation ratios that are generally found in the material. Our results suggest that control over electrical properties will be facilitated by avoiding thermal discontinuities during the preparation of crystals. In addition, very slow cooling procedures may present a way to decrease compensation in CuInSe₂ films, used for solar cells, so as to help efforts to improve their open-circuit voltages.

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Step Coverage Prediction in Low-Pressure Chemical Vapor Deposition

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A mathematical model incorporating simultaneous one-dimensional Knudsen diffusion and chemical reaction is employed to analyze transient behavior during low-pressure chemical vapor deposition (CVD) in features of arbitrary geometry on patterned semiconductor wafers. For a given feature geometry and CVD reaction, the dimensionless model equations reveal that step coverage is controlled by the value of a single dimensionless parameter that represents the ratio of a characteristic deposition rate to a characteristic reactant diffusion rate. Temperature, reactant partial pressure at the feature mouth, and aspect ratio are the process parameters that may be varied to improve step coverage for a given CVD chemistry. The proper directions of change for temperature and reactant pressure are determined by the parameters of the intrinsic reaction rate expression for the particular CVD chemistry of interest. Deposition of amorphous SiO₂ from TEOS (tetraethyl silicate) is considered as a specific example. The model predicts that step coverage improves with decreasing temperature and increasing pressure of TEOS at the feature mouth, in agreement with experimental results. Calculation of reactive sticking coefficients shows that this diffusion-reaction model is consistent with the modification of the line-of-sight model that invokes low sticking coefficients to explain conformal step coverage.

Introduction

An important goal of chemical vapor deposition (CVD) of thin films in microelectronics fabrication is conformal step coverage over patterned regions of the wafer. Examples of processes in which step coverage is especially critical include deposition of insulating films between metal interconnect levels and deposition of metal, silicide, or polysilicon films for the electrical interconnections themselves. Current trends in very large scale integration (VLSI) technology make achievement of conformal step coverage increasingly important for several reasons. First, as lateral dimensions have continued to shrink, vertical dimensions have not scaled by the same factor, due primarily to materials' properties limitations.¹ Hence aspect ratios of contact holes and vias have steadily increased. Second, because chip area is largely controlled by metalization area, vertical integration in the form of multilevel interconnection has been adopted as a strategy for further shrinking of microcircuits.^{1,2} Poor step coverage and lack of planarity in underlying deposited layers will compound the problem of achieving good step coverage in subsequently deposited layers.

It has been previously reported³⁻¹⁰ that the quality of step coverage in low-pressure CVD (LPCVD) depends on deposition parameters including temperature, total gas-flow rate, reactant pressures, and growth rate as well as the substrate material and the geometry of the step. The currently accepted theory used to explain experimental observations, summarized briefly in the next section, borrows heavily from the ideas and experience of physical

vapor deposition. In this model it is presumed that LPCVD is a line-of-sight process and that therefore non-conformal step coverage can largely be explained by geometrical shadowing effects. The model in its current form cannot quantitatively predict the proper relationship between deposition parameters. Moreover, in certain instances the model incorrectly predicts even qualitative directional changes in step coverage (improvement vs degradation) as a particular parameter is varied. These major shortcomings have led to much confusion in the field and have dictated programs of development that are empirical in nature.

Alternative models for gas-solid reaction on internal surfaces exist in the literature but have not gained much attention. In 1957, Peterson¹¹ modeled atmospheric pressure carbon gasification in a long cylindrical pore with simultaneous first-order reaction and diffusion. In a series of papers published in the late 1970s, van den Brekel and

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