temperature and pressure. X is dependent on the distinction between regions with weak and strong cohesion. The system is nevertheless easy to memorize and it fulfils the basic requirement of being less complicated to describe than the group of objects that it is applicable to.

More important than any classification is that this scheme offers the preparative researcher a systematic way of thinking about possible new materials. If we want to find new sorbents extending the range of pore sizes found in zeolite-type 3(Y) materials, the X(0) classes with closed pores are of no interest and this leaves 9 classes. Inspection of Figure 1 suggests that 2(Y) materials with truly two-dimensional SUs and 0(Y) materials with Y = 2 to 0 are unlikely candidates for new microporous solids, because they involve structural units of complicated shape that in some cases must be arranged in a very precise fashion.

The remaining types of solid, i.e. 1(3), 1(2), 1(1) and 0(3), are represented by three rod packings and a sphere packing in Figure 1, and these four types seem to be the most feasible alternatives, since voids are automatically produced when rounded 1- or 0-dimensional SUs are packed. In order to obtain a narrow pore size distribution, all SUs must have the same diameter and the packing must exhibit a high degree of order. The most easily achieved arrangement of SUs is probably some form of close-packing. A look at the geometry of close-packed arrangements of spheres or cylindrical rods reveals that a pore diameter of ≥ 10 Å requires an SU diameter of ≥ 65 Å for these two types of 0(3) and 1(1) materials. The void fractions of these two arrangements are 26 and 9 vol.-%, respectively, and do not depend on the diameter of the SUs. Supercrystals of close-packed, surfactant-covered nanospheres of iron oxide have been studied by electron microscopy.[16]

The less dense 0(3) and 1(1) packings depicted in Figure 1 have void fractions of 48 and 21 vol.-%, and require an SU diameter of 24 Å, in order to exhibit 10 Å pores. A number of more complicated rod packings, of which two are shown in Figure 1 in order to illustrate the 1(2) and 1(3) classes of solid, have been described by O'Keeffe and Andersson.[11]

In conclusion, analysis of the possible combinations of connectivity exhibited by pores and structural units, according to the proposed scheme, suggests that regular arrangements of uniform nanocylinders or nanospheres could constitute a family of microporous solids, extending the range of pore dimensions observed in zeolite-type materials. The simple X(Y) scheme of classification used in this note can easily be extended to include more complicated cases, like XY(Z) or X(Y)(Z). For example, a hypothetical 02(2) material such as fullerene-intercalated graphite could be an interesting target for synthesis.

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A Model for the Successful Growth of Polycrystalline Films of $CuInSe_2$ by Multisource Physical Vacuum Evaporation

By *Reiner Klenk, Thomas Walter, Hans-Werner Schock,** and *David Cahen*

Solar cells based on $CuInSe_2$ (CISe) polycrystalline thin films are one of the few realistic alternatives to (poly)crystalline Si for small- and large-scale practical solar energy conversion to electricity.[1,2] The great potential of CISe for solar energy conversion is due to its direct band gap, high absorption coefficient, good thermal, environmental and electrical stability and the existence of a variety of potential low-cost methods for its preparation. The last point is also valid for complete cells. Efficient (>14%) devices based on CISe/CdS heterojunctions (cf. Fig. 1) have been prepared and have shown no evidence of degradation with time.[2,3] The spectral match of the absorber to the solar spectrum, as

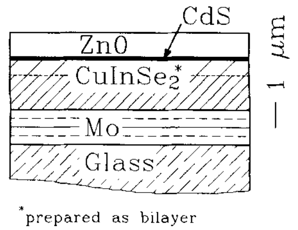

Fig. 1. Schematic cross-section of a $CuInSe_2$/CdS/ZnO thin-film solar cell.

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well as the built-in potential at the heterojunction can be improved by alloying CISe with $CuGaSe_2$ (CGSe)[4] or $CuInS_2$ (CIS),[5] which increases the band gap.

Absorber growth technologies for highly efficient solar cells are based on selenization of precursor films[6, 7] or on multi-source physical vacuum evaporation.[8] On the basis of detailed investigations of the growth of CIS(e) and CGSe films prepared by the latter method, and of solar cells based on them, we have derived a model that explains the role of secondary copper-chalcogenide phases in thin-film formation. This model is considered a key-point in understanding the underlying causes for the success of the so-called "BOEING recipe"[8] for film preparation and recent modifications thereof.[9] This method was originally meant to prevent Cu-nodule formation.[10]

It is well known that several properties of $Cu–III–VI_2$ materials undergo a sudden change as soon as even a small amount of excess copper ($Cu/III > 1$) is present in the material. In accordance with the pseudo-binary phase diagrams,[11–13] this is attributed to the formation of copper-chalcogenide secondary phases, which are degenerate p-type semiconductors and dominate the opto-electronic and surface properties of Cu-rich films. They are thus unsuitable as absorbers in photovoltaic cells. A more precise model of their microstructure has evolved from structural characterization, etching experiments and surface analyses.[14–17] According to these studies, Cu-rich material consists of nearly stoichiometric chalcopyrite grains with good opto-electronic quality and mainly $Cu_{2-x}Se$ (CuS, in the case of CIS) segregated at grain surfaces. There are, however, also observations that did not lend themselves to straightforward explanation up to now. In Cu-rich films the individual grains are significantly larger than in Cu-poor films and their size is also less dependent on substrate temperature.[18] In CISe these grains are (112) oriented (up to a certain Cu-excess), whereas Cu-deficient CISe films exhibit (220)/(204) orientation.[19] Comparison of the stable-growth polyhedron, derived from estimations of surface energy, with the observed morphology suggests that isotropic growth occurs only in Cu-rich films.[20] The conclusion that we draw from the latter results is that the growth mechanism is modified by the presence of copper-chalcogenides.

As has been recognized in an early stage of the development of CISe, single-layer absorbers do not result in optimum cell performance. This has been overcome by the empirical approach of depositing a bilayer, i.e. Cu-poor on Cu-rich—the above-mentioned BOEING recipe.[8] Until recently the explanation of the benefits of this approach was thought to be as follows:[8, 19, 21–28] By depositing Cu-poor onto Cu-rich materials one can get the former to also grow as large, rather than as the normally small crystallites. Because the top layer also inherits the preferred orientation of the Cu-rich film, this suggests some type of epitaxial growth of the, otherwise poorly formed, Cu-poor films. Compositional equilibration takes place during the process, resulting in removal of the secondary phase from the bottom layer. The coarse grained morphology is desirable because large crystallites lead to smaller interface area and to fewer grain boundaries within the absorber. In addition, transmission electron microscopy studies have shown that these films are also superior with respect to internal defects such as twinning and stacking faults.[29, 30] This will minimize deleterious recombination at the heterojunction and in the absorber, leading to better collection of photogenerated carriers (current density, fill factor) and decreased bucking currents (open circuit voltage).

In summary, the BOEING recipe takes advantage of the large grains in Cu-rich films and combines this with the absence of secondary phases in Cu-deficient ones. Although additional aspects, such as optimization of bulk and surface defect-chemistry and band line-up at grain surfaces, may play a certain role, we agree that this is a prime result of the BOEING recipe. Nevertheless, there is experimental evidence that this type of epitaxy alone does not provide a complete explanation of film growth in bilayers. Undisturbed top-layer growth and preservation of the bottom layer's morphology have been observed in CGSe and CISe under a variety of experimental conditions as long as the amount of Cu-poor material deposited was such that the overall composition was still Cu-rich. Beyond this point, however, a new nucleation—and a change in growth mechanism—have often been observed. In this case, small crystallites with the triangular shape known from Cu-deficient films start to grow.[24] This is accompanied by a steady increase in 220/204 peak intensities in X-ray diffraction (XRD). In CGSe this change in growth mechanism is somewhat more expressed. These observations lead to the assumption that the composition of the bottom layer is of importance for top layer growth, which has been verified by the following experiments. Cu-rich bottom layers of CGSe were etched in aqueous cyanide solutions, which selectively removes the $Cu_{2-x}Se$ and results in a film with "Cu-rich morphology" but stoichiometric composition. A top layer deposited onto them grows with "Cu-poor morphology" unless it is Cu-rich by itself. Simple chemical etch, without composition change, did not affect the bottom layer's ability to yield top layer growth with good morphology. In a control experiment a Cu-poor CGSe layer has been deposited onto substrates coated with a thin layer of copper, which resulted in "Cu-rich morphology". We will show here and argue that this composition dependence reflects the need for the presence of a Cu–Se phase to get the good, Cu-rich morphology.

If we assume that the $Cu_{2-x}Se$ phase identified in Cu-rich films after cool down is also present during preparation, and in view of the above-mentioned microstructural model of Cu-rich films, we can consider epitaxial growth of the ternary on the binary phase $Cu_{2-x}Se$. Lattice matching between $Cu_{2-x}Se$ and CISe can be expected because all phases are based on face centered cubic packed Se lattices and because the lattice constant for cubic $Cu_{2-x}Se$ is 574 pm and those for tetragonal Cu_2Se are 1152/1152/1174 pm, while for CISe they are 578/578/1162 pm, i.e. a good match. However, the results from experiments where the formation of a Cu–Se phase was provoked by excess Cu in different stages of film growth and where a Cu-poor ternary has been deposited afterwards argue against this idea. In that case any remaining Cu-excess is found to exist, after cooling down to room temperature, as $Cu_{2-x}Se$ on the surface of the grains and no $Cu_{2-x}Se$ is found after cool down if a sufficient thickness of the Cu-poor ternary was deposited.

In one of these experiments a bottom layer was deposited by evaporating Cu and Se only. Keeping Se flux and substrate temperature (490 °C) constant and the shutter opened, the Cu-source was cooled down and the Ga source simultaneously ramped up to deposit a top layer of only Ga and Se. The total amount of Ga evaporated was slightly less than the amount of Cu. After cool-down the film was quickly transferred to a UHV system for X-ray photoelectron spectroscopy (XPS) to determine the surface composition. XRD analysis shows that the resulting film consists of $CuGaSe_2$ together with a small amount of $Cu_{2-x}Se$. No Ga–Se phases have been detected. This implies that the Cu–Se phases of the bottom layer had been consumed to form $CuGaSe_2$.

XPS shows the surface of the film to be Cu-rich (Table 1). The Cu-Auger parameter, shape and position of the Cu $2p_{3/2}$ peak are the same as in Cu-rich films grown with constant rates and are an indication of a Cu–Se compound on the surface.[15, 23] Wavelength dispersive X-ray spectroscopy (WDX) shows that the bulk material is stoichiometric while near the surface it is Cu-rich (Table 1). This means that a compositional gradient exists which is opposite to that expected from the preparation sequence. These findings cannot be explained by simple epitaxy. Instead of this we have to assume that copper-chalcogenides are an intermediate state in the growth of Cu-rich films, where it makes no difference if the Cu-excess has its origin in the vapor or in the substrate (from an earlier deposited bottom layer). In contrast to this, for Cu-poor films, the growth is determined directly by arrival rates and sticking coefficients of vapor-phase species. Further evidence is obtained from an experiment where ...CISe/CGSe/CISe... multilayers have been made (100 nm each layer, experimental details are given elsewhere[31]). They are found to intermix completely, leading to a uniform quaternary phase, as long as Cu-rich ternaries are deposited. When Cu-poor ternaries are deposited, no intermixing is observed (by XRD).

Table 1. Bulk and surface composition of a CGSe thin film prepared by depositing Ga–Se on top of Cu–Se.

Measurement	% Cu	% Ga	% Se	Ga/(Cu + Ga)
WDX 25 kV	25.1	25.3	49.5	0.50
WDX 15 kV	24.7	25.2	50.0	0.50
WDX 5 kV	26.6	24.0	49.4	0.48
XPS	39.0	9.3	51.6	0.19

The model, that we propose to explain the link between composition and growth mechanism is based on the following assumptions: 1) The presence of a low-temperature liquid Cu–Se phase. 2) The growth is aided by this liquid phase. 3) At least In and Se (or an In–Se phase) dissolve in the liquid phase.

With these assumptions we propose that, after initial nucleation, the ternary chalcopyrite grains grow by way of a vapor–liquid–solid mechanism (VLS[32]). The vapor species condense at the surface of the binary phase covering the grains. They are then transported to the binary/ternary interface where the crystallite is growing (Fig. 2). The growing grain will be nearly stoichiometric. If the vapor is deficient in Cu the Cu–Se phase will be gradually consumed. If excess Cu is present in the vapor the amount of Cu–Se will increase. These processes take place at the deposition temperatures of 350 °C/450 °C (bottom/top) for CISe and up to 650 °C for CGSe. We note that the absorber of the currently best CISe-based cell has been grown at a higher temperature (550 °C,[9]).

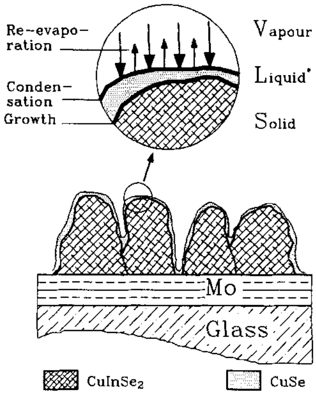

Fig. 2. Model of the growth process in the presence of a CuSe binary phase. *Liquid or surface quasi-liquid (see text).

In the absence of a true ternary phase diagram, we will use the binary ones[33] to justify the assumption of a low temperature liquid phase. In Figure 3 we have drawn the three relevant binary phase diagrams, Se–Cu, Cu–In, In–Se, following the representation of the Cu–Ga–Se system by Mikkelsen.[13] We note the existence of liquid Cu–Se and In–Se phases at temperatures close to those used for thin-film growth. For In–Se there is a monotectic point at 520 °C at 31.5 at.-% Se, for Cu–Se at 523 °C for Cu:Se ≈ 1:1. In both cases there are liquid immiscibility regions, with those towards In-rich compositions in In–Se and towards Se-rich compositions in Cu–Se being of particular interest because of the temperatures involved. Following the reasoning of Mikkelsen[13] for the Cu–Ga–Se system we can expect a liquid immiscibility region to extend across this portion of the Cu–In–Se ternary diagram, and to have a low-temperature liquid composition in that portion.

Based on this analysis the existence of liquid (or surface quasi-liquid) Cu–Se, In–Se or Cu–In–Se phases is possible during the growth process. From the observation that Cu-excess leads to improved morphology, it is clear that the Cu–Se phase is the most important one, at least during early stages of bilayer growth (assumption 1). According to the pseudo-binary phase diagrams, excess In can be incorporated in the chalcopyrite phase. This is not so for Cu, which may explain why a surface liquid phase is more easily formed in this case, since a driving force to keep the excess Cu at the surface exists and the Cu–Se binary phase diagram may be valid also in the presence of the third element. Also, the composition of the Cu–Se liquid is more favorable for the formation of $CuInSe_2$ than are those of the In–Se liquids (selenium deficiency). The latter argument is emphasized by the fact that the thermodynamic driving force for $CuInSe_2$ formation from Cu_2Se and In_2Se_3 is minimal, while that for formation from CuSe and InSe is considerable.[34] This makes it likely that one or both members of the latter pair of binaries play a role. This is further supported by the fact that CuSe or InSe molecules can be formed already in the gas phase.[34]

From the experimental point of view, the clearest indications for the presence of a liquid film during preparation have been found in films of pure Cu–Se, prepared under conditions similar to those used for the preparation of the chalcopyrite, i.e. a substrate temperature of 490 °C and Se-overpressure. Even at an average thickness of half a micrometer these films do not completely cover a glass substrate, which may be explained by formation of droplets during the evaporation. Substrate artefacts, like scratches or dust, provoke liquid contraction (coagulation) as indicated by the observed irregularities in film growth in their vicinity. Likewise, if the substrate is partly covered with molybdenum the liquid is torn apart by liquid contraction close to the Mo-edge, leading to a area several micrometers wide where the substrate is not covered by a film (Fig. 4). A similar effect has been found in Cu-rich CGSe films, where a "trench" runs parallel to the Mo-edge. Inside the trench the film is thinner and composed of small stoichiometric grains, in contrast to the bigger Cu-rich grains in the environment. Although more pronounced at higher substrate temperatures this irregularity is present also in films grown at a lower (480 °C) substrate temperature.

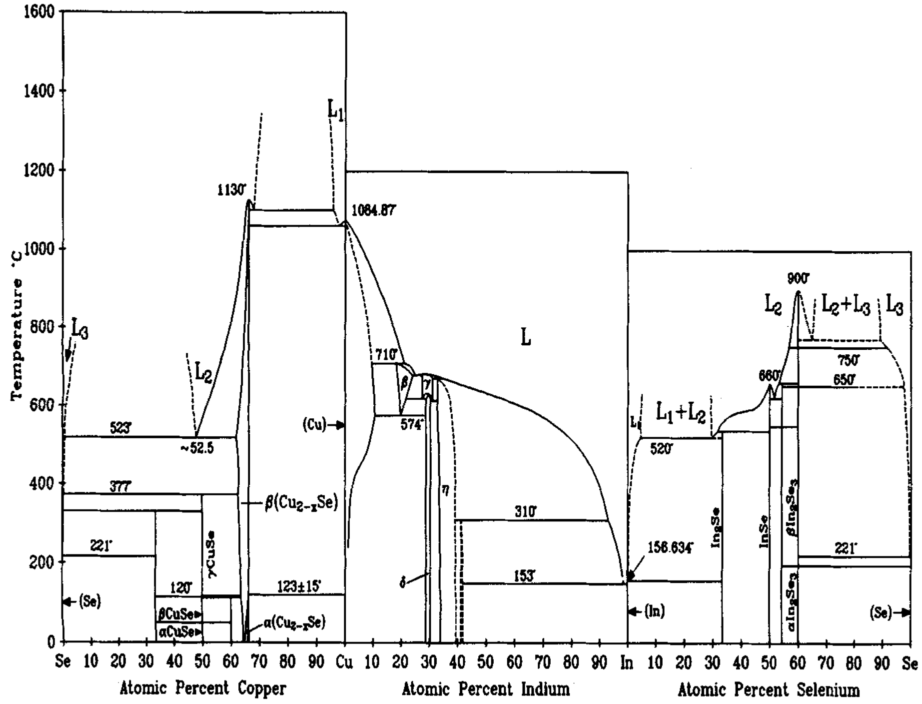

Fig. 3. Cu–Se, Cu–In, and In–Se binary phase diagrams [33].

As in pure Cu–Se, irregular film growth induced by substrate artefacts, e.g. accumulation of material where the substrate is scratched, has often been observed and is attributed to liquid contraction. Cu–Se films grown at 490 °C on glass exhibit a high density of whiskers (Fig. 5) which is a strong indication of VLS growth.[32] In Cu-rich CISe films the interaction between the solid and the liquid phase seems to be different. In that case we find a "string" of big Cu-rich grains at the Mo-edge and a high density of whiskers on the adjacent, non-metallized glass.

There seems to be a contradiction between the assumption of a Cu:Se $\approx$ 1:1 phase involved in the growth and the lack of evidence for a solid CuSe (1:1) phase at room temperature. Rather, one can identify the $Cu_{2-x}Se$ phase in Cu-rich films. The reason is the monotectic reaction $L_2 \rightleftarrows \beta\text{-Cu}_{2-x}\text{Se}_s + L_3$, which occurs at 523 °C for Cu:Se ≈ 1:1. This reaction can be rewritten approximately as $2\ \text{CuSe}_{liq} \rightleftarrows \beta\text{-Cu}_2\text{Se}_s + \text{Se}_{liq}$. In our case (low pressure and Se source switched off after preparation) the Se probably evaporates, thus shifting the equilibrium more to the right. This process occurs above the limit of stability of CuSe, which is at 377 °C. While at that temperature the peritectic reaction $\beta\text{-Cu}_2\text{Se}_s + L_3 \rightleftarrows \gamma\text{-CuSe}$ can occur, it does not take place under the conditions that prevail when that temperature is reached during cooling (lack of L_3). However, in the case of Cu–In–S film growth we find CuS, rather than Cu_{2-x}S, as secondary phase. This is understandable since the above-mentioned peritectic reaction occurs in the Cu–S system at a temperature closer to the growth temperature than is the case for the Cu–Se system.

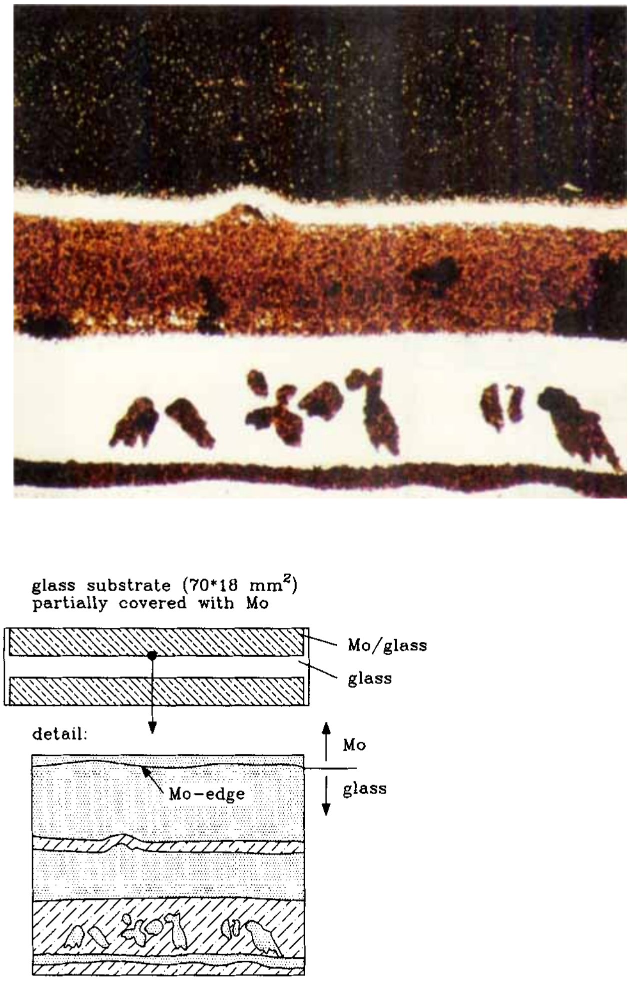

Fig. 4. Top) Optical transmission micrograph (× 500) of a Cu–Se film on glass close to the Mo-edge. Color differences are due to different phases. Bottom) Schematic of a Cu–Se film on a partially metallized glass substrate.

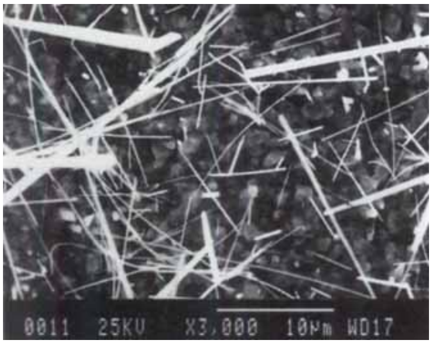

Fig. 5. SEM micrograph of a Cu–Se film on glass.

Experimentally, these ideas have been confirmed in films of pure Cu–Se by preparing a sample with normal cooling (same cooling rate as in preparation of the ternary) and an additional one, where the sample was quenched by venting the vacuum chamber with pure dry nitrogen up to about 0.5 bar immediately after closing the shutter. The phases identified by XRD were not the same in both samples, supporting the assumption that reactions occur during cool-down. As should be expected from the reactions given above, the Cu/Se ratio, as determined by EDS, was slightly lower in the quenched sample (Cu/Se = 1.35 vs. Cu/Se = 1.47). The sample with normal cooling shows the XRD spectrum of Cu_{2-x}Se plus small amounts of an unidentified phase. Since the film's Se content is higher than that of pure Cu_{2-x}Se and since the intensity of the XRD maxima is rather low, it is conceivable that amorphous Se-rich Cu–Se is present. This holds also for the quenched sample, which in addition shows low intensity reflections from Se and CuSe. In this case the (re-)evaporation of Se has been partly suppressed by the high-pressure ambient, so that crystalline Se as well as crystalline CuSe (via the peritectic reaction) have formed. In Cu-rich ternary films we have not been able to detect higher Se contents with accelerated cooling, probably due to insufficient quenching rates. It has not been possible to increase the Se content by post deposition annealing at 377 °C in Se flux indicating that the peritectic reaction requires the presence of L_3 or at least very high Se pressures, neither of which is present during normal cool-down.

Our model explains the morphology of Cu-rich films and their microstructure. It is evident that the non-interrupted growth after switching to Cu-deficient vapor and the compositional equilibration in the bilayer process share a common origin and cannot be viewed as different processes, epitaxy and interdiffusion, as was the case in earlier models. If the latter were correct a layered structure of Cu–Se, CGSe and Ga–Se should have formed in the Ga–Se on top of Cu–Se experiment, while our model predicts CGSe grains with Cu_{2-x}Se on them, in accordance with the experimental results. Furthermore, the failure of epitaxial top layer growth onto etched bottom layers is not compatible with previous assumptions but is easily explained by the model introduced in this contribution. We can explain the extensive intermixing between In and Ga in the multilayer experiment by assuming that more material from the vapor is buffered in the binary phase than is evaporated during one cycle, or that at the temperature of deposition we have still a facile equilibrium between ternaries and binaries. Another interesting experimental observation, viz. an increase in lattice parameters of CGSe by about 0.15% (and similar results in CISe[35]) after removal of $Cu_{2-x}Se$ secondary phases by cyanide treatment can be explained by the VLS model, if we assume that upon cooling and resulting solidification of Cu-rich CGSe compressive stress is exerted on the crystallite, (part of) which was covered by the liquid. This idea is supported by the observed narrowing of XRD peaks, after cyanide treatment of CGSe. It should be noted that leaching out of Cu from the ternary cannot explain this observation because it should lead to compression rather than expansion of the lattice as can be seen from the data presented in the literature.[36]

Naturally, the weak points of the proposed model are the use of (equilibrium) phase diagrams for a non-equilibrium growth process, on the one hand and the absence of true ternary phase diagrams at the temperatures of interest on the other hand (cf. ref. [37] for some limited information and ref. [11] for a tentative, pseudo-binary, T-x diagram, down to relatively low temperatures, incorporated in the phase diagram of ref. [12]). The phase diagrams show that the substrate temperatures used in the BOEING recipe for CISe are below the temperatures where we can expect liquid phases in equilibrium. However, the surface temperature may be higher than the bulk temperature because of the energy of the particles in the vapor and the exothermic reactions involved in the formation of the compound.[34]

The actual temperature can be less than the bulk melting point, as long as the thin surface layer is molten, or at least sufficiently close to it to allow efficient mass transport. $T_{melt} \times 0.3$ (in K) has been suggested as minimum temperature required for making surface defects mobile.[38] On Cu metal, liquid-like surface mobility is found, experimentally, at $T_{melt} \times 0.7$ (in K).[39] In the solid, mass transport of Cu and Ag is very efficient in Cu–X and Ag–X (X = S, Se, Te) phases already at relatively low temperatures.[10,40] This is true also for $CuInSe_2$ and $CuGaSe_2$.[41,42] Because there is a Se-rich atmosphere during evaporation/growth, and because there is a miscibility gap between L_2 and L_3, it is conceivable that in addition to the Cu-rich (L_2) Cu–Se phase we have a Se-rich liquid, L_3, to provide the liquid at even lower temperatures, but the low sticking coefficient of Se makes it unlikely that this phase plays a major role.

Without doubt further experiments are necessary in order to refine the model. Nevertheless, the three fundamental steps, viz. condensation at the surface of the binary, transport to the growth planes and growth at the binary/ternary interface are compatible with all our experimental findings and are considered to be valid independent of complete understanding of the underlying mechanisms for each step.

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