Amorphization reaction in thin films of elemental Cu and Y

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Compositionally modulated thin films of Cu and Y were prepared in an ultrahigh-vacuum dc ion-beam deposition chamber. The amorphization reaction was monitored by *in situ* x-ray-diffraction measurements. Growth of amorphous $\text{Cu}_{1-x}\text{Y}_x$ is observed at room temperature with the initial formation of a Cu-rich amorphous phase. Further annealing in the presence of unreacted Y leads to Y enrichment of the amorphous phase. Growth of crystalline CuY is observed for $T=469$ K. Transmission-electron-microscopy measurements provide real-space imaging of the amorphous interlayer and growth morphology. Models are developed, incorporating metastable interfacial and bulk free-energy diagrams, for the early stage of the amorphization reaction.

I. INTRODUCTION

It has been clear for some time that a sensitive interplay of kinetic and thermodynamic effects is operative in the early stages of the interdiffusion reactions of thin-film diffusion couples. An increased interest in these effects has followed the discovery that amorphous phase formation can occur before the formation of equilibrium crystalline phases and that solid-state amorphization reactions (SSAR) present an alternative to the conventional routes for metallic glass formation.¹⁻⁴ The later stages of the amorphization reaction can be conveniently understood in terms of bulk metastable free-energy diagrams.⁴ For sufficiently long reaction times and sufficient amorphous phase growth, a metastable equilibrium condition prevails with an equality of the chemical potential of an element within locally coexisting phases.^{5,6} Due to the absence of routine experimental probes of sufficient depth resolution, the earliest stages of the amorphization reaction have been much less studied. Recent experiments, however, demonstrate that the amorphization reaction may be characterized by several stages and that the kinetic pathway leading to the final metastable equilibrium may itself manifest additional metastable equilibria.

Schröder, Samwer, and Köster reported observations of the very early stage of the amorphization reaction of Co and Zr.⁷ Transmission-electron-microscopy measurements revealed the initial growth of an amorphous phase with composition greatly enriched in the early transition-metal component. In this interdiffusion reaction, Co is the dominant moving species.^{3,8} Initial formation of a Co-rich amorphous phase parallels the typical initial formation in metal-silicide interdiffusion reactions of a phase that is rich in the moving species.⁹ Subsequent experimental work in the Co-Zr system indicated a sample-preparation-dependent initial course of the amorphization reaction.^{3,10,11}

We have recently reported the occurrence of a solid-state amorphization reaction in the Cu-Y system.¹² We now describe this reaction in greater detail. *In situ* x-ray-diffraction measurements were performed to monitor

the real-time sequence of the amorphization reaction. These measurements were performed immediately following sample deposition and without exposure of the sample to the atmosphere. Cross-section transmission-electron-microscopy measurements provide real-space imaging of the growth morphology of the amorphous phase. Growth of an amorphous phase enriched in the early transition-metal atom is observed. We develop modes for the early stage of the Cu-Y amorphization reaction that incorporate available thermodynamic and kinetic information.

II. EXPERIMENTAL

Compositionally modulated Cu-Y multilayer samples were prepared by dc ion-beam sputtering using 1-keV Ar^+ , a background Ar pressure of 5×10^{-5} torr, and a chamber base pressure in the low 10^{-8} -torr range. A description of the sample preparation chamber is contained in Ref. 13. A Nb buffer layer with thickness 30 Å was deposited onto a clean, buffered-HF-etched, and ion-etched Si(111) substrate to eliminate possible interaction between the Si and the Cu-Y sample. Y (target purity 99.9%) and Cu (target purity 99.999%) were alternately deposited with a typical deposition rate of 1.0 Å/s. Lateral uniformity of the sample was ensured by rotating the substrate during deposition. The substrate was nominally at room temperature. A total film thickness of near 2000 Å was deposited. A Cu layer was always deposited last to serve as a barrier to the oxidation of Y during subsequent handling.

Immediately following deposition, representative samples were transferred by means of *in situ* manipulator drives to the x-ray-diffractometer chamber of the vacuum system.¹³ Samples were then annealed, with an x-ray chamber pressure of 10^{-7} torr, on the x-ray hot stage. The course of the interdiffusion reaction was monitored by high-angle x-ray-diffraction measurements in the symmetric-reflection geometry. Cu $K\alpha$ radiation with a 1° divergence angle, 0.15° collection angle, and a typical counting time of 10 s per angular increment was used.

Transverse-electromagnetic (TEM) measurements on selected samples allowed real-space imaging of the growth morphology of the amorphous phase. TEM samples were prepared in cross section by standard grinding and argon-ion milling at 4 keV with liquid-nitrogen cooling. To minimize oxidation after ion milling, the samples were then immediately loaded into a Philips EM 430 TEM operated at 300 keV. TEM samples experienced a temperature of about 120°C for 1 h during preparation.

III. RESULTS

A. X-ray diffraction

Figure 1 shows a series of *in situ* x-ray-diffractometer scans taken from a sample with $\lambda=300$ Å and overall composition $\text{Cu}_{50}\text{Y}_{50}$. The thermal history of the respective scans is indicated in the inset annealing sequence. Sample deposition required 30 min and was complete at time $t=0$. Peaks corresponding to crystalline hcp Y and fcc Cu are present in the as-deposited sample. Preferred crystal growth in directions orthogonal to close-packed planes is evidenced by the dominant presence of the Y(002) and the Cu(111) reflections. We attribute the broad maximum at $2\theta\sim 35^\circ$ to an amorphous component in the sample. This broad maximum is present for the

FIG. 1. X-ray-diffractometer scans taken at various stages in the anneal of a sample with composition modulation wavelength $\lambda=300$ Å and overall composition $\text{Cu}_{50}\text{Y}_{50}$. The thermal history of the respective scans is noted in the inset annealing sequence.

as-prepared sample and indicates that a significant amount of reaction has occurred during sample deposition. The decline in intensity with annealing time of the crystalline Y and Cu reflections provides a measure of the consumption of these elemental components; we infer a corresponding growth of amorphous $\text{Cu}_{1-x}\text{Y}_x$ from the absence of Bragg peaks that can be associated with crystalline phase formation.

The Cu and Y reflections are observed to decline in intensity with time at 300 K, indicating a room-temperature onset for the amorphization reaction. Complete consumption of Cu occurs after annealing for 3 h at 337 K. The presence of unreacted Y at this stage indicates that the initially formed amorphous phase is enriched in Cu.

A further decline in intensity of the Y Bragg peaks occurs at higher annealing temperatures and indicates an Y enrichment of the initially formed amorphous phase. A pronounced shift of the Y(002) peak towards lower scattering angles is observed to accompany further amorphization. Crystalline CuY (Ref. 14) in the CsCl (*B2*) structure is observed to grow at an annealing temperature of $T=469$ K. Coinciding with the growth of crystalline CuY is the complete disappearance of the hcp Y(100) and (200) reflections. The absence of these peaks is a signature for an hcp to fcc transformation of the crystal structure of the remaining Y metal (see below). The rather broad peak that appears in scan H of Fig. 1 at $2\theta=42^\circ$ is consistent with an onset of growth of crystalline Cu_2Y .¹⁴

These trends are quantitatively summarized in Fig. 2 where the normalized peak areas of the combined Y(100) and (002) reflections, Cu(111), and the combined CuY(100) and (200) reflections are plotted as a function of annealing time and temperature. We attribute the sharp initial decrease for times 0–5 h in the Cu and Y peak areas at room temperature to a slightly elevated sample

FIG. 2. Normalized peak areas of the combined Y(100) and (002) reflections (X's), Cu(111) (diamonds), and the combined CuY(100) and (200) reflections (boxes) as a function of annealing time and temperature. Lines have been drawn to guide the eye.

temperature immediately following deposition. A further decline in intensity at room temperature is evident over the 20 h following deposition. The nonlinear decline in Y intensity at $T=337$ K indicates a crossover to diffusion-limited growth of the amorphous phase. Growth of crystalline CuY at $T=469$ K is diffusion limited.

A series of samples were prepared with composition modulation wavelength λ varied from 75 to 500 Å and with overall composition $\text{Cu}_{50}\text{Y}_{50}$. These samples were then annealed at room temperature. The presence of unreacted elemental Cu was detected only for $\lambda \geq 300$ Å. Excess Y metal was evident in each of these samples. With decreasing λ , a transformation from the bulk-equilibrium hcp Y structure to the fcc Y structure¹⁵ is observed. Systematic shifts with λ of the d spacings of the hcp Y(100) and (002) peaks and of the fcc Y(111) peak are illustrated in Fig. 3. For comparison, bulk-equilibrium hcp Y has (100) d spacing of 3.15 Å and (002) d spacing of 2.86 Å.

B. Transmission electron microscopy

Electron micrographs taken from samples prepared in cross section show alternating amorphous and crystalline layers. Figure 4 shows a TEM bright-field (BF) pair and diffraction pattern of the as-prepared Cu-Y

FIG. 3. X-ray-diffractometer scans upon samples with varying composition modulation wavelength λ and with overall composition $\text{Cu}_{50}\text{Y}_{50}$ showing the transformation from hcp to fcc Y with decreasing λ . The d spacings of the hcp Y(100) (diamonds) and (002) (crosses) and the fcc Y(111) (crosses) are shown in the inset as a function of λ . The elemental Y thickness in these partially amorphized samples is less than 0.74λ .

sample with composition-modulation wavelength of 150 Å and overall composition $\text{Cu}_{50}\text{Y}_{50}$. The electron diffraction pattern of the multilayer allowed identification of strongly textured fcc Y (Ref. 15) (Fig. 4 inset) and amorphous $\text{Cu}_{1-x}\text{Y}_x$ (Fig. 5). When viewed with the dominant orientation of the Y grains in a [110] projection, {111} twinning of the fcc Y is revealed. The DF image formed from a (111) reflection¹⁶ (indicated by the arrow in Fig. 4 inset) clearly shows the range of grain sizes and shapes. The orientation relationship between crystalline Y grains in layers separated by amorphous $\text{Cu}_{1-x}\text{Y}_x$ in this reacted sample is consistent with the initial presence of crystalline Cu in the as-deposited film. The relative thickness of the amorphous phase and of the

FIG. 4. TEM bright-field (BF), dark-field (DF) pair and diffraction pattern of the as-prepared Cu-Y sample with composition-modulation wavelength of 150 Å and overall composition $\text{Cu}_{50}\text{Y}_{50}$. The light regions in the BF image correspond to fcc Y metal and the grey mottled regions correspond to amorphous $\text{Cu}_{1-x}\text{Y}_x$. An estimated composition of the amorphous phase $\text{Cu}_{70}\text{Y}_{30}$ is obtained from the relative thickness of the amorphous phase and of the unreacted Y. The DF image was formed from the Y(111) reflection that is noted by an arrow in the inset diffraction pattern. Nonplanar growth of amorphous $\text{Cu}_{1-x}\text{Y}_x$ and a marked rounding of the Y grains is evident in the DF image.

unreacted Y allows an estimate of $\text{Cu}_{70}\text{Y}_{30}$ for the composition of the amorphous phase in this sample.

Figures 6(a) and 6(b) show high-resolution images of the observed growth morphology. $\{111\}$ lattice fringes of the fcc Y can be resolved and show that the SSAR has resulted in a nonatomically smooth reaction front. Growth of amorphous $\text{Cu}_{1-x}\text{Y}_x$ is observed both at the original Cu/Y interface and between grains of the elemental Y. This latter observation is described in detail in Ref. 12.

IV. DISCUSSION

A. Amorphization reaction of an elemental A-B diffusion couple

Typically one element *A* is the dominant moving species in the amorphization reaction of an elemental A-B diffusion couple.^{8,17} Element *A* moves into the *B* lattice leaving defects in the *A* lattice. We consider the following growth sequence for the amorphization reaction:

Interdiffusion of *A* into the *B* host lattice leads to a nonequilibrium concentration of *A* in *B*. Relaxation of the *B* lattice occurs with formation of an amorphous layer at the *A/B* interface initially and at the *B*-amorphous interface with succeeding phase growth. With increasing thickness of the amorphous layer the amorphous phase

FIG. 5. Diffraction pattern taken from the grey mottled region of the BF image of Fig. 4 showing the diffuse ring pattern characteristic of amorphous $\text{Cu}_{1-x}\text{Y}_x$.

relaxes into a bulk metastable equilibrium. Further annealing leads to the formation of equilibrium crystalline $A_{1-x}B_x$ phases. In the following, we describe the course of the SSAR of Cu and Y in terms of the characteristic time scales τ_i in this reaction sequence. For previous discussions of the SSAR process, see Refs. 1–3 and 18.

FIG. 6. High-resolution phase-contrast images of the amorphous-crystalline boundary region. $\{111\}$ lattice fringes of the fcc Y can be resolved and show that the SSAR has resulted in a nonatomically smooth reaction front with the reaction proceeding into the region between Y grains (indicated by the arrows).

Previous workers have characterized the bulk metastable equilibrium state in terms of a free-energy diagram that is characteristic of the bulk supercooled liquid. Shown in Fig. 7 is the bulk metastable free-energy diagram for the Cu-Y system that was calculated using the procedures of Schwartz and Johnson⁴ (see Ref. 3 for details.) The negligible equilibrium solubility of Y in elemental Cu and of Cu in elemental Y (Ref. 14) is schematically indicated in Fig. 7. The common-tangent construction has been used to determine the composition limits of coexisting phases. The intersection of the common-tangent line with the free-energy axis determines the chemical potential of Cu for $x=0.0$ and the chemical potential of Y for $x=1.0$ in the represented phases.

We have recently described a procedure for estimating the free energy associated with an incremental layer of amorphous material in contact with an elemental crystal.¹² In Fig. 8 are shown the free energies that we obtain for an amorphous $\text{Cu}_{1-x}\text{Y}_x$ layer with thickness $t=2.5$ Å in contact, respectively, with elemental Cu and Y. The thickness chosen for this interfacial layer corresponds roughly to 1 monolayer of material and can be viewed as an approximate lower bound on the thickness of a physically realizable amorphous layer. For thicknesses larger than about 5 Å the free energy of the interfacial layer is well described in terms of the bulk metastable free-energy diagram (Fig. 7). For comparison Fig. 8 also shows values for one-half of the free energy of a high-angle grain boundary in Y metal, $\frac{1}{2}\gamma_{\text{SS}}^{\text{YY}}$, and in Cu metal, $\frac{1}{2}\gamma_{\text{SS}}^{\text{CuCu}}$, and the interfacial energy associated with a crystalline, nonepitaxial Y/Cu interface, $\gamma_{\text{SS}}^{\text{CuY}}$,¹⁹ that were calculated following Miedema and Broeder.¹⁹

Figures 7 and 8 allow an approximate determination of

FIG. 7. The Gibbs-free-energy change for formation of amorphous $\text{Cu}_{1-x}\text{Y}_x$ at $T=300$ K from the pure elements at 300 K. A negligible solubility of Y in elemental Cu and Cu in elemental Y is schematically indicated. Application of the common-tangent rule determines the composition limits of coexisting phases.

FIG. 8. The Gibbs-free-energy change for formation of a thickness $t=2.5$ Å of amorphous $\text{Cu}_{1-x}\text{Y}_x$ in contact with elemental Cu $\Delta G(x)t + \gamma_{\text{SL}}^{\text{Cu}(\text{Cu}_{1-x}\text{Y}_x)}$ and in contact with elemental Y $\Delta G(x)t + \gamma_{\text{SL}}^{\text{Y}(\text{Cu}_{1-x}\text{Y}_x)}$. Also shown are values for one-half of the interfacial energy associated with a high-angle grain boundary in pure Y metal, $\frac{1}{2}\gamma_{\text{SS}}^{\text{YY}}$, and in pure Cu metal, $\frac{1}{2}\gamma_{\text{SS}}^{\text{CuCu}}$, and the interfacial energy associated with the original Y/Cu interface, $\gamma_{\text{SS}}^{\text{CuY}}$.

the compositions of bulk and interfacial amorphous layers with minimum free energy. Values that we obtain for amorphous compositions of minimum free energy at the Cu- and at the Y-amorphous phase boundaries, for a given relative supply of Cu and Y, are shown in Table I. These values will provide a qualitative basis for the following discussion.

B. Early stage

The growth limitation in the early stage of the amorphization reaction is thought to arise at either the A- or B-amorphous interface due to a finite rate for atomic transport across the interface or to a reaction barrier at the interface.²⁰⁻²² Diffusive transport of the mobile atomic species across the growing amorphous interlayer occurs faster than growth of the interlayer. This interfacial limitation upon growth can be viewed as a constraint on the relative supply of A and B.

For experimental time scales τ_{expt} such that

$$\tau_L < \tau_G < \tau_{\text{expt}} < \tau_E,$$

the bulk metastable-free-energy diagram provides an appropriate description of the amorphization process. Since diffusive transport of the mobile atomic species across the growing amorphous interlayer occurs faster than growth of the interlayer, a uniform amorphous composition is expected. Essentially, in this regime the amorphous interlayer is saturated with the component whose supply is nonlimiting. The composition of this amorphous phase follows from the bulk metastable-free-energy

TABLE I. Compositions x of the amorphous phase $\text{Cu}_{1-x}\text{Y}_x$ that result from the calculated metastable-free-energy diagrams for an interfacial amorphous layer in contact with the elemental metals and for a bulk amorphous layer. Constraints upon the relative supply of Cu and Y are noted.

	Relative supply	Interfacial metastable free-energy diagram x	Bulk metastable free-energy diagram x
Cu-amorphous	excess Cu	0.23	0.21
interface	excess Y	1.0	0.64
Y-amorphous	excess Cu	0.0	0.21
interface	excess Y	0.40	0.64

diagram. Compositions resulting for the Cu-Y system that are obtained from Fig. 7 are summarized in Table I. If the supply of Cu is limiting, a uniform composition $x \sim 0.64$ is predicted. If the supply of Y is limiting, a uniform composition $x \sim 0.21$ is predicted. This model does not explicitly depend upon the relative atomic mobilities of the reacting elements.

If growth of the amorphous phase occurs faster than relaxation into bulk metastable equilibrium then minimization of the bulk metastable free energy is no longer possible. We consider a second case with time scales such that

$$\tau_I < \tau_G < \tau_{\text{expt}} < \tau_L, \tau_E.$$

Since $\tau_I < \tau_G$, we may minimize the free energy of an interfacial layer of the amorphous phase in contact with the elemental metal. If the composition of this interfacial layer is metastable on time scales long with respect to further amorphous phase growth, then formation of a bulk amorphous layer with composition characteristic of the interfacial layer occurs. In contrast to the previous case, this model requires a specification of the growth interface and so of the dominant moving species in the reaction. The composition of the bulk amorphous phase follows from minimization of the free energy appropriate to an amorphous interfacial layer at the B-amorphous interface. Compositions resulting for limiting cases in the Cu-Y system are summarized in Table I. It has been observed without exception that the smaller late transition-metal atom is the dominant moving species in the SSAR of early, late transition-metal pairs.^{8,17,23} We may then assume that Cu is the dominant moving species in the SSAR of Cu-Y so that amorphous phase formation occurs at the Y-amorphous phase boundary. An amorphous composition $x \leq 0.40$ is predicted independent of the relative supply of Cu and Y.

We now have two models for the initial state of the amorphization reaction: The experimentally observed initial formation of a Cu-rich amorphous phase follows from a growth-limiting supply of Y to the amorphous layer, or, alternatively, from identification of Cu as the dominant moving species in the reaction. By experimentally altering the interface, and so the relative supply condition, between the as-deposited elemental metals it may be possible to experimentally distinguish between these two models.

C. Later stages

For larger layer thicknesses, amorphous phase formation is limited by the rate for atomic transport across the amorphous interlayer. Thermodynamic coupling across the interlayer is inhibited by this timescale for diffusive transport. In this stage of the reaction, local metastable equilibrium conditions apply at each interface of the amorphous phase with the elemental metals.⁶ With completion of the reaction, a homogeneous amorphous phase is predicted with compositions determined by overall metastable equilibrium.

For these longer-time later-stage processes the bulk metastable free-energy diagram is thought to apply:⁴

$$\tau_L < \tau_{\text{expt}} < \tau_E.$$

For the Cu-Y system, coexistence of elemental Y and an amorphous phase with composition $x \sim 0.64$ is predicted from Fig. 7.

In Figs. 1 and 2, we observe continued reaction of crystalline Y following the complete consumption of crystalline Cu. The decline in intensity of the Y Bragg reflections is nonlinear with annealing time and indicates a diffusion-limited growth of the amorphous phase. For this sample with overall composition $\text{Cu}_{50}\text{Y}_{50}$ we expect all of the remaining Y metal to react. Before complete amorphization of Y occurs, however, we observe the interceding growth of crystalline CuY. This last reaction corresponds to

$$\tau_E < \tau_{\text{expt}}.$$

Equilibrium free-energy considerations are now appropriate.

Figures 7 and 8 allow a systematic description of thermodynamic driving forces that are operative in the amorphization reaction of Cu and Y. Depending upon the relationship between the time scales for growth and for compositional relaxation, the early stage of the reaction is described in terms of the metastable free-energy diagram for a bulk amorphous interlayer (Fig. 7) or in terms of the free-energy diagram for an interfacial amorphous layer in contact with elemental Y metal (Fig. 8). These models allow an identification of experimental parameters that influence the initial course of the reaction. After initial formation of a Cu-rich amorphous phase, the amorphous composition relaxes in response to the varia-

tion in supply of the elemental components. Compositional relaxation of the amorphous phase competes with relaxation into equilibrium crystalline phases. Experimentally, we observe the formation and growth of crystalline CuY before the amorphous phase obtains the metastable state with minimum free energy that is indicated by Fig. 7.

V. CONCLUSIONS

The course of the amorphization reaction of Cu-Y multilayer thin-film samples was monitored by *in situ* x-ray-diffraction measurements. Room-temperature growth of an amorphous $\text{Cu}_{1-x}\text{Y}_x$ phase was observed. The initially formed amorphous phase has a composition that is enriched in Cu. Following the consumption of Cu, continued amorphization of the remaining Y metal is observed. With decreasing thickness of the remaining Y metal, x-ray-diffraction measurements indicate a transformation from the bulk equilibrium hcp Y structure to the fcc Y structure. Growth of crystalline CuY occurs with further annealing at $T=469$ K. The growth morphology

of the amorphous $\text{Cu}_{1-x}\text{Y}_x$ phase was observed in cross section by transmission electron microscopy. A laterally nonuniform reaction front is observed with reaction proceeding preferentially into the grain boundaries of the Y metal. Models are developed for the early stage of the amorphization reaction that incorporate calculated metastable, bulk and interfacial, free-energy diagrams.

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FIG. 4. TEM bright-field (BF), dark-field (DF) pair and diffraction pattern of the as-prepared Cu-Y sample with composition-modulation wavelength of $150 \text{ \AA}$ and overall composition $\text{Cu}_{50}\text{Y}_{50}$. The light regions in the BF image correspond to fcc Y metal and the grey mottled regions correspond to amorphous $\text{Cu}_{1-x}\text{Y}_x$. An estimated composition of the amorphous phase $\text{Cu}_{70}\text{Y}_{30}$ is obtained from the relative thickness of the amorphous phase and of the unreacted Y. The DF image was formed from the Y(111) reflection that is noted by an arrow in the inset diffraction pattern. Nonplanar growth of amorphous $\text{Cu}_{1-x}\text{Y}_x$ and a marked rounding of the Y grains is evident in the DF image.

FIG. 5. Diffraction pattern taken from the grey mottled region of the BF image of Fig. 4 showing the diffuse ring pattern characteristic of amorphous $\text{Cu}_{1-x}\text{Y}_x$.

FIG. 6. High-resolution phase-contrast images of the amorphous-crystalline boundary region. $\{111\}$ lattice fringes of the fcc Y can be resolved and show that the SSAR has resulted in a nonatomically smooth reaction front with the reaction proceeding into the region between Y grains (indicated by the arrows).