Surface-induced ordering: A model for vapor-deposition growth of amorphous materials

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During vapor deposition growth of amorphous materials, we propose that adatom clusters align such as to minimize surface energy. This alignment, a thermally activated process, causes the as-grown structure of the amorphous thin film to be anisotropic and stabilizes the structure against subsequent relaxation, presumably by reducing free volume. A two-level-systems analysis describes the effect of deposition temperature, deposition rate, and subsequent annealing. The model is used to describe the growth-induced magnetic anisotropy of amorphous Tb-Fe.

Vapor deposition is used to prepare a wide variety of amorphous materials. Qualitatively, these materials possess many of the same properties as those prepared by other techniques such as liquid quenching,[1–3] but certain properties, such as the perpendicular anisotropy of the amorphous rare-earth transition metal (*a*-RE-TM) alloys, depend critically on the vapor deposition process.[4–6] The effect on the amorphous structure of this process (e.g., deposition rate and substrate temperature during deposition) is, however, not well understood, although it is clearly possible to prepare amorphous materials using a wide range of temperatures.[6,7] Simulation work has primarily focused on macroscopic effects, such as columnar microstructure or surface roughness, or whether the material is amorphous or crystalline, rather than on the as-grown local or intermediate range structure. Simulation techniques which might give local structure are limited by computer time; molecular dynamics simulations are forced to use unphysically rapid deposition rates, while ballistic aggregation simulations are forced to limit surface mobility to unphysically low values. Annealing of an amorphous material, whether prepared by vapor deposition or other technique, at temperatures too low for crystallization, tends to eliminate the "memory" of preparation technique and results in both reversible and irreversible structural changes, commonly referred to as relaxation.[1,2,8–10] Relaxation can be described by a two-level-systems model in which the atomic rearrangements require thermal activation over an energy barrier, with a distribution of barrier heights and potential energy well depths due to the wide range of local environments in an amorphous structure.[8,9]

It was recently shown that in certain conditions, the effect of increasing substrate temperature during deposition is qualitatively different than the effect of annealing, the former enhancing a local "memory" of the growth direction while the latter eliminates it.[6] We propose that changes in the as-grown structure of an amorphous material with deposition temperature and rate can be modelled within a *surface* two-level-systems analysis, similar to that used for annealing. A crucial difference is that the broken symmetry of the surface inherently leads to an *anisotropic* structure while annealing (in the absence of applied fields or stresses) leads to an *isotropic* structure. Local structural units are assumed to be formed at the growth surface from the deposited atoms or ions. These are initially randomly oriented but can lower the surface free energy by reorienting into energetically favorable configurations, somewhat analogous to a surface reconstruction for a crystalline film. The high ratio of surface to bulk mobility under most vapor deposition growth conditions then traps this anisotropic structure into the film.

The potential energies of two surface states involved in a single reorientation are shown schematically in the inset of Fig. 1. The lower energy state may simply maximize the number of bonds for all surface atoms or may require a more element-specific arrangement of the atoms. In either case, it represents an orientational alignment of local structural units with respect to the growth surface and hence the occupancy of state 2 causes a growth-induced anisotropy in the structure. The fractional occupancy of state 2, n_2, is taken approximately equal to 0 initially and that of $n_1=1$ (i.e., the configurations are initially randomly oriented). The reorientation requires activation over an energy barrier E_b. The rate of change of n_1 is given by

$$\frac{dn_1}{dt} = -\nu n_1 \exp(-E_b/kT_s), \tag{1}$$

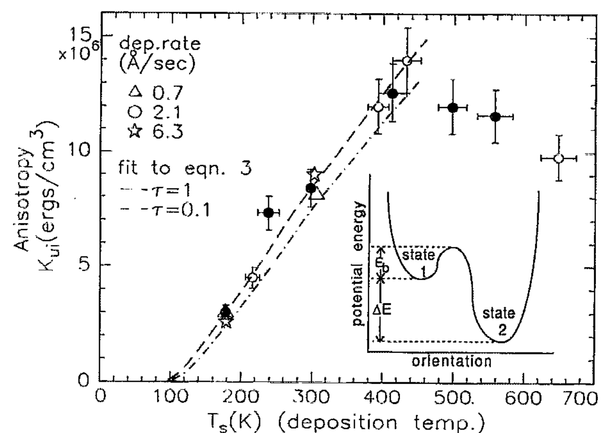

FIG. 1. Magnetic anisotropy of 2000-Å-thick electron beam coevaporated a-$Tb_{28}Fe_{72}$ vs substrate temperature during deposition. Deposition rates are shown in legend. Lines shown are fits to Eq. (3) for two deposition rates. Solid symbols show samples used for annealing. Representative error bars are shown for 2.1 Å/s samples. Insert: Two-level analysis of surface states during growth. State 1: Initial, randomly-oriented configuration. State 2: Oriented configuration, maximizes coordination of surface atoms.

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assuming $E_b+\Delta E \gg kT_s$ (i.e., neglecting reversible processes), where ν is the attempt frequency, and T_s the substrate temperature during deposition. If τ is the time to deposit one monolayer, the final occupancy of state 2 is

$$n_2=1-n_1=1-\exp\{-\tau\nu \exp(-E_b/kT_s)\}. \quad (2)$$

Assuming a *distribution* of barrier heights $D(E_b)$, due to a wide range of state 1 depths, the anisotropy in the structure, which is proportional to n_2, is then given by

$$A=A_0\int_0^{\infty} D(E_b)[1-\exp\{-\tau\nu \exp(-E_b/kT_s)\}]dE_b. \quad (3)$$

In the work to be presented here, we will assume a flat distribution, i.e., $D(E_b)$=constant, over some range of energy. This expression then predicts that the anisotropy will show a thermally activated dependence on deposition temperature and a logarithmic dependence on inverse deposition rate.

The reorientation minimizes surface energy by maximizing coordination, causing the surface and therefore the final structure to contain less free volume. As a result, energy barriers to structural relaxation in the bulk of the film are higher. Put simply, the higher the original growth temperature, the more resistant the structure is to subsequent relaxation, and perhaps to crystallization. We will present data in this letter for the anisotropy of a structure and its relaxation but we suggest more generally that the density of as-grown vapor deposited amorphous materials can be predicted by a surface two-level-system analysis. A similar model but with a single barrier height was previously proposed to describe the deposition temperature dependence of certain (isotropic) properties of *a*-Ge, including in particular the density.[11]

This anisotropic structure and its relaxation is most easily probed using a magnetic system. Thin films of alloys such as *a*-Tb-Fe possess a large uniaxial magnetic anisotropy perpendicular to the film plane, a property critical to their present use as magneto-optic recording media.[4,5] These alloys possess large *local* single ion magnetic anisotropy due to the nonspherical rare-earth ion. If the amorphous structure were isotropic, this local anisotropy would vary in direction from rare-earth site to site, averaging to zero. The perpendicular growth-induced anisotropy results from an orientational correlation of the local anisotropy fields due to an anisotropy in the chemical and/or topological short range order.[12] Although the magnetic anisotropy is large and easily measured, the underlying structural anisotropy has proven far more difficult to resolve. Extensive structural analysis of these alloys has been made over a number of years by many techniques;[13–16] evidence of anisotropy has recently been claimed by two groups.[15,16] No evidence of microcrystallinity was found in any of these studies.

Thin films of *a*-$Tb_{28}Fe_{72}$ (Curie temperature $T_c \approx 400$ K) have been prepared by electron beam coevaporation in an ultrahigh vacuum deposition system. The films were protected from oxidation by a Nb underlayer and a Nb/Al bilayer on top.[17]. Annealing was performed in a vacuum furnace at a pressure of 1×10^{-6} Torr. The room-temperature values for the magnetic moment and anisotropy of these samples were determined by standard techniques using

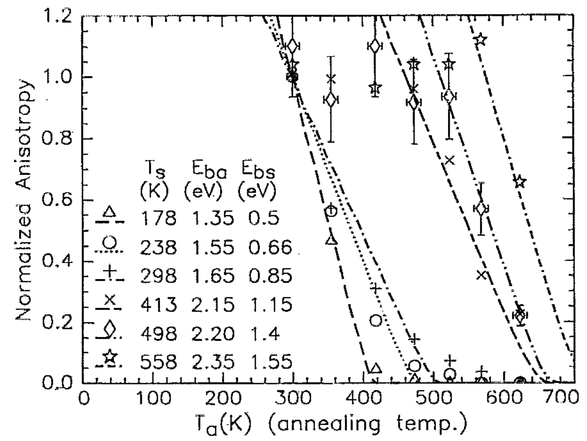

FIG. 2. Relaxation of magnetic anisotropy with annealing for *a*-Tb-Fe films grown at different T_s. Annealing time is 4 h at each temperature. Data for each T_s are normalized to the initial value. Representative error bars are shown for T_s=300 K. Lines are fits to two-level relaxation model: τ=4 h, $\nu=8\times10^{12}$ s^{-1}, $D(E_b)$=constant from 0 eV to upper cutoff E_{ba}. Insert: E_{ba} and E_{bs} vs T_s; E_{bs} is the highest energy barrier overcome in creating the anisotropy at the surface during the growth $\tau\nu \exp\{-E_{bs}/kT_s\} \ll 1$).

torque and vibrating sample magnetometers.[6] There is no dependence of magnetic moment or T_c (within the error bars of the measurements) on deposition temperature or annealing.[6] Figure 1 shows the dependence of the intrinsic uniaxial anisotropy constant K_{ui} on deposition temperature and rate.[18] Consistent with previous observations,[6] the anisotropy increases strongly with increasing deposition temperature up to approximately 500 K where a rollover is seen. It is independent of deposition rate from 0.7 to 6.3 Å/s, within the error bars of the measurements. We have fit this data to the model using Eq. (3) for two different deposition rates: τ=1 and 0.1 for an attempt frequency $\nu=8\times10^{12}$ s^{-1}.[19] Up to 500 K, the strong dependence on deposition temperature is fit remarkably well. The model predicts a very weak (logarithmic) dependence on deposition rate, consistent with observations. A log-time dependence in deposition rate is difficult to observe experimentally, particularly as faster depositions may result in heating of the substrates. The fit shown required a lower cutoff of 0.3 eV in the distribution $D(E_b)$. This cutoff may physically be due either to a real minimum in the energy barriers or to an energy dependence of A_0 in Eq. (3), i.e., the magnetic anisotropy may not couple equally to all atomic arrangements. The rollover at 500 K will be discussed below.

Figure 2 shows the dependence of the anisotropy on *annealing* temperature for films grown at various *deposition* temperatures. Consistent with previous observations of annealing, the anisotropy for all films decays as the structure relaxes towards the isotropic state which is the minimum energy configuration for the bulk amorphous structure.[20] The magnitude of the anisotropy for each deposition temperature is normalized to its initially measured value (shown with solid symbols in Fig. 1). Figure 2 shows that the higher the original growth temperature, the more resistant the structure is to subsequent relaxation. Films grown at or below room temperature show significant relaxation at even the lowest annealing temperature, and a strong inverse correlation of the

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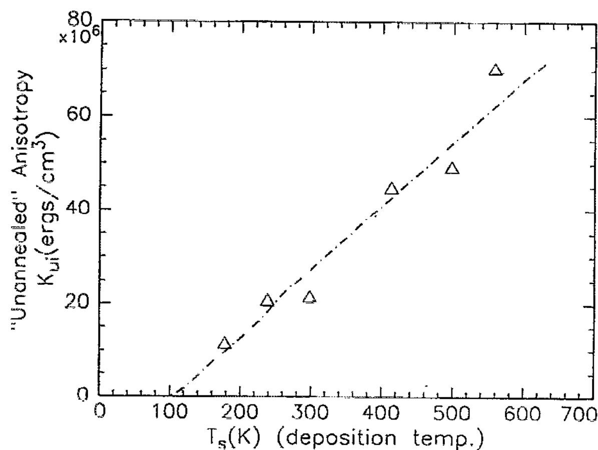

FIG. 3. Theoretical values for anisotropy vs growth temperature assuming no relaxation in the bulk of the structure. Line shown is fit to Eq. (3) for $\tau=1$, $\nu=8\times10^{12}$ s^{-1}, and $D(E_b)$=constant from 0.3 eV up.

annealing temperature at which all anisotropy has vanished with the original growth temperature. Films grown above room temperature show no relaxation of the anisotropy until the annealing temperature reaches the original growth temperature, above which they too begin to relax.

Using the standard two-level model for structural relaxation,[8,9] we have fit the annealing data, assuming a flat distribution of activation energies up to an upper cutoff E_{ba}, determined fundamentally by the annealing temperature at which the anisotropy vanishes. The deviations from the fits, particularly evident for the low T_s materials, imply either that the energy distribution is not in fact flat, or more likely, that the distribution shifts upwards with annealing, i.e., that the annealing process itself fills in vacancies and therefore increases E_{ba}. The energy barriers to relaxing the anisotropic structure for each film are much higher than the energy barriers surmounted in creating the anisotropy in that film during the growth. For example, a film grown at T_s=300 K at 3.5 Å/s surmounted a maximum energy barrier (defined as E_{bs}) of 0.85 eV $\{\tau\nu\exp(-E_{bs}/kT_s)\ll1\}$ while to completely relax the anisotropy involved energies up to 1.65 eV. Without this difference, the anisotropy would relax in the bulk of the sample as fast as it is created at the surface and thus would never have been observed! Physically, the difference in these energy barriers occurs because of higher coordination in the bulk than at the surface. E_{bs} and E_{ba} are shown in the insert of Fig. 2.

It is clear from Fig. 2 that all films shown in Fig. 1 were subject to relaxation before they were even measured, both during growth and on bringing T_s<300 K samples to room temperature. We have used the fits shown in Fig. 2 to determine a theoretical value for the anisotropy, assuming no relaxation. These values are shown in Fig. 3; they show the same thermally activated behavior as the measured values of Fig. 1 except that there is no rollover at 500 K, suggesting that the rollover is a result of the inevitable annealing which occurs during the growth.

In conclusion, we propose that both the as-grown structure of vapor-deposited amorphous materials and its subsequent relaxation are controlled by the formation and alignment of adatom clusters at the surface during the growth such as to minimize surface energy. We have shown that the effect of raising the deposition temperature is qualitatively different than the effect of annealing. A two-level-systems model for the atomic rearrangements predicts the observed dependence of the as-grown structure on deposition temperature, rate, and how the subsequent relaxation depends on the original growth temperature. It should be emphasized that as in all such models for the amorphous phase, whether describing low temperature thermal properties or structural relaxation, such a model gives insight into the process but does not identify the actual structural units involved in the rearrangements. An important consequence of this work is that the amorphous phase can be stabilized by growing it at the highest possible temperature without allowing appreciable crystallization to begin.

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