

## Chemically Induced Step Edge Diffusion Barriers: Dendritic Growth in 2D Alloys

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(Received 10 January 1996)

To investigate the effects of multiple film components on the morphology of thin films, the growth of Co and Ag on Ru(0001) has been studied by scanning tunneling microscopy. Two types of growth have been identified. In the first, the Co from the vapor phase is directly incorporated into existing Ag islands. In the second, islands composed of a Co-Ag mixture are formed by etching of the existing pure Ag islands. These two mechanisms, which occur simultaneously, lead to dramatically different morphologies. In the second case, dendritic growth of the alloy is found despite the fact that neither of the component metals alone exhibit this behavior. We attribute the dendritic growth to chemically induced step edge diffusion barriers which must generally exist in multicomponent film growth. [S0031-9007(96)00411-5]

PACS numbers: 68.35.Ct, 68.35.Bs, 81.15.Kk, 81.65.Cf

The controlled growth of multicomponent films is becoming an increasingly important field of epitaxy, yet little is known about how chemical differences in the film materials affect growth properties. An important aspect to consider is the effect of the complex chemical environment experienced by an adatom as it attaches to a growing island of a multicomponent system. The details of this incorporation process are known to have a determining influence on the shape of the clusters, i.e., whether the islands are compact or ramified, which often defines the film structure and morphology at later growth stages. In the simpler case of single component epitaxy, much progress has been made in understanding these effects, and the conditions leading to ramified growth have been extensively studied [1–7]. Ramified growth generally results from the reduced mobility of atoms once they attach to islands, a process known as diffusion limited aggregation (DLA) [8]. In this Letter we report on a fundamental chemical effect that enhances ramified growth in multicomponent films. This effect is observed in the atomic layer dendritic growth of alloy islands made of Ag and Co on Ru(0001). Individually, these overlayer metals do *not* exhibit dendritic morphologies under the same growth conditions. The alloy island shapes are found to be intimately linked to the internal structure of the alloy and is a striking example showing that the kinetics of two-dimensional alloy growth can be greatly affected by the energetics of alloy formation. We propose a model to explain this growth behavior in which the alloy formation is the key to driving the dendritic growth by creating edge diffusion barriers whose heights are related to the relative binding energies of two components on the surface. This additional diffusion barrier generally exists in cases of multicomponent metal film growth and is expected to be an important factor in determining their growth morphologies.

The experiments were performed in a UHV chamber with a base pressure less than  $10^{-10}$  Torr. Ag was de-

posited by evaporation from a resistively heated tungsten basket while Co deposition was achieved via direct current heating of a Co wire. The films described in this paper were grown in the following sequence. Ag was first deposited at room temperature followed by an anneal to 550 °C. This produces compact islands of Ag attached to the lower edges of Ru steps. Co was then evaporated onto the sample at temperatures described in the text below. As has been shown by several groups, STM is able to distinguish different metals within the same layer [9,10] and Ag was consistently imaged approximately 0.2 Å higher than Co for the imaging conditions used. All STM data was acquired in the constant current mode and displayed in gray scale representation.

Various studies have shown that Ag and Co individually do not mix with Ru when deposited onto the (0001) surface [11–13]. In addition, the bulk phase diagram of Ag and Co exhibits a substantial miscibility gap. However, many such systems have been recently shown to produce surface alloys [10,14–16]. In the present case, because of the opposite signs of the strains imposed upon Ag and Co by the Ru(0001) substrate, mixing, in the form of a strain relieved alloy phase, is favored [10]. Depositing 0.25 ML of Co onto a surface containing 0.25 ML of Ag produces a film shown in Fig. 1(a). At this coverage, only monolayer islands form. Several features can be noticed immediately. First, within this large scale image, the curved edges of the original Ag islands can still be identified. This is partially marked in Fig. 1(a) by a heavy black line. Two different types of island shapes can be found on either side of this boundary. Type A islands (as we will refer to them) possess dendritic shapes and have nucleated on the Ru terraces away from the edges of the original Ag islands. The shape of the islands clearly reflect the threefold symmetry of the substrate this structure and can also be found attached to the edge of the original Ag islands. The other type of island is found in the areas that were originally covered by Ag prior to Co deposition

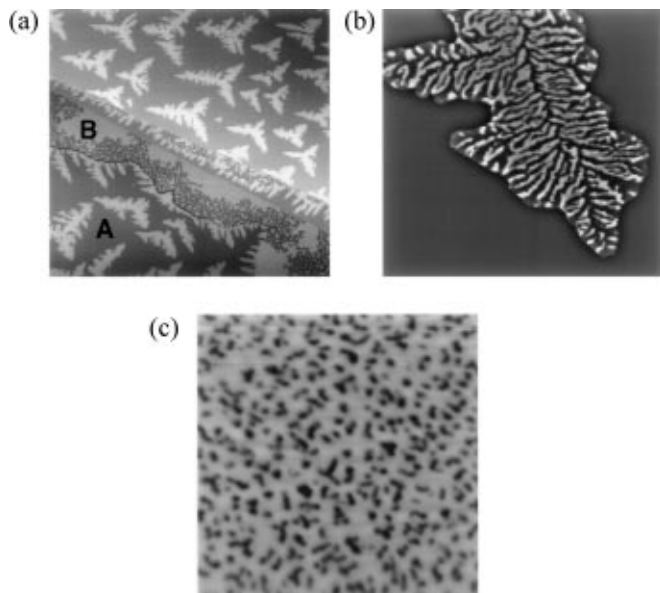


FIG. 1. (a)  $7500 \times 7500 \text{ \AA}$  image of a Co-Ag alloy grown at  $70^\circ\text{C}$  as described in the text. (b)  $500 \times 500 \text{ \AA}$  image of a type A dendritic island. (c)  $400 \times 400 \text{ \AA}$  image of type B islands.

[see the region of Fig. 1(a) marked with a “B”]. They contain large voids in which the Ag has been displaced, revealing the bare Ru substrate. In contrast to the type A islands, type B islands have a compact shape.

Upon closer inspection, it is clear that both types of islands are made up of a mixture of Co and Ag as is shown in Figs. 1(b) and 1(c). The cluster shapes of the Co and Ag within the two morphologies of islands, however, are quite different. In the compact type B islands, Fig. 1(c) the Co form small clusters of about  $10\text{--}20 \text{ \AA}$  in width. In addition to these small compact clusters of Co, more linear clusters could often be found, again with the width of about  $10 \text{ \AA}$ . Within the dendritic islands (A), Co and Ag form alternating “veins” that run throughout the island [Fig. 1(b)] in patterns very reminiscent of veins in a leaf. The veins extend in the  $\sqrt{3}$  directions and are similar in width to the size of the small Co clusters in the compact islands.

To understand the formation of two types of islands, one must consider the two types of areas onto which the deposited Co can arrive: (i) onto an existing Ag island or (ii) onto the bare Ru terrace. In the first case, the Co impinging on the existing Ag islands directly incorporates into the Ag lattice and results in the formation of the type B of islands. In the other situation, Co deposited onto the Ru(0001) surface diffuses along the surface and undergoes nucleation and growth process to form the dendritic type A islands. The question remains as to how the Ag combines to form the dendrites. We believe that both Ag and Co are incorporated into these islands via condensation into the alloy phase from a dilute 2D gas phase. The Co gas phase is produced from the deposition,

while the dilute Ag gas is in equilibrium with the Ag solid islands. The existence of such an equilibrium 2D gas has been found on several surfaces to be responsible for a range of dynamic phenomena [17–19]. On the Ag(100) surface, gas phase Ag adatoms have been shown to even drive island diffusion at room temperature [20]. Recent work by Nohlen *et al.* [21] has used measurements the density of the Ag gas phase on Ru(0001) at higher temperatures to deduce Ag-Ag interaction energies.

This picture accounts for the formation of the voids in the original Ag islands because the original Ag islands supply the adatoms necessary to maintain the Ag partial pressure in the 2D gas. This mechanism is similar to the Ostwald ripening of islands [22] where an island covered surface lowers its free energy by the islands exchanging atoms with an adatom gas phase: Large islands have lower chemical potential than the adatom gas and thus gain atoms, while small islands have large chemical potential and thus loose atoms. In our case, the chemical potential of the alloy phase is smaller than that of the pure Ag solid, leading to Ag transfer to the alloy. This mass transfer effectively “pumps” Ag from the pure phase to the alloy phase. Simultaneous to the pumping of Ag, Co deposited onto the Ag also forms the alloy and has a stabilizing influence in those randomly located areas. This competition results in the void networks found in the type B islands. This model is further corroborated by the fact that as the deposition of Co is continued beyond the point at which there is no remaining pure Ag phase, growth of all islands is purely due to Co addition [23].

We next focus on the mechanisms responsible for the dendritic islands. This is an especially intriguing issue since neither Co nor Ag grown individually on Ru(0001) exhibits dendritic growth. Most of the Co atoms deposited onto the regions of the substrate where type A islands form, initially land and migrate on the Ru substrate. Interaction with Ag then arises in a purely 2D fashion that leads to the dendritic islands with the vein structure. Closer inspection of the dendritic islands indicate a close relationship between the irregular shape and the internal vein structure of Co and Ag. Furthermore, the width of the island fingers is made up of veins growing in a  $60^\circ$  orientation from the direction of the finger growth. Both the vein structure and the dendritic island shapes are due to kinetic limitations as indicated by annealing experiments. Heating the film of Fig. 1 to  $325^\circ\text{C}$  leads to the formation of compact Ag-Co alloy islands of a specific stoichiometry [23]. Further insight into the relationship between the internal and external structures can be obtained through a series of experiments in which the Co was deposited with the substrate held at higher temperatures. Images of films produced at temperatures of  $138$  and  $170^\circ\text{C}$  are shown in Figs. 2(a)–2(d). From this data, one can see that as the growth temperature increases, the dendritic nature of the islands relaxes as the continuity of the internal

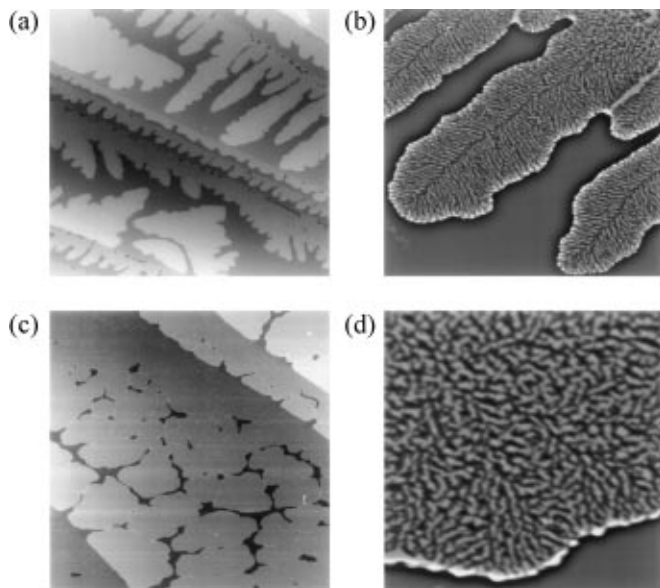


FIG. 2. (a)  $6000 \times 6000 \text{ \AA}$  image of a Co-Ag alloy grown at  $138^\circ\text{C}$  as described in text. (b)  $1750 \times 1750 \text{ \AA}$  image of the vein structure with the finger islands of (a). The image is contrast enhanced, so that the intensity difference between the Co and Ag represents a corrugation height of about  $0.2 \text{ \AA}$ . Note the integrity of the veins. (c)  $10000 \times 10000 \text{ \AA}$  image of a Co-Ag alloy grown at  $170^\circ\text{C}$ . Islands now exhibit compact shapes as described in text. (d)  $600 \times 600 \text{ \AA}$  image of the internal structure with the islands of (c). Continuous vein structure no longer exists at this growth temperature.

veins is reduced until one reaches a situation of compact islands [Figs. 2(c) and 2(d)]. It is important to note that both the dendritic growth and the internal vein structure are removed at the *same* temperature. Clearly, these two phenomena are linked and will be a key factor in developing our model below.

From the evidence described above, we develop a model as to the influence of the alloying phenomena on the dendritic growth of the alloy islands. Dendritic growth in metal films has been observed in many cases and is due to the lack of edge diffusion. The annealing experiments described above indicate that this is also the case for our system. Since neither Ag nor Co alone exhibit edge diffusion limitations leading to irregular growth, the key question is how the edge mobility is altered by the formation of the mixed phase. As has been shown in the case of Cu and Ag on Ru(0001) [10], the immiscible combination forms alloys on the surface of the substrate, resulting in a strain relieved structure which stabilizes the alloy. This is also applicable to the present case of Ag and Co since the Ru substrate imposes a strain of opposite sign on the two overlayer metals. A mixture results in a better lattice match to the substrate, thereby reducing the strain energy. However, the energetic cost of such an alloy is the formation Ag-Co bonds at the interface between the two materials, which are weaker than Ag-Ag and Co-Co bonds. A balance is reached

between this interfacial energy and the strain relief that determines the length scale of the cluster sizes [14,24,25]. This length scale persists even in the annealed films which exhibit a preferred stoichiometry and cluster size distribution. However, the fact that at lower temperatures they form into veins is a kinetic process linked to the dendritic growth. We propose the following scheme for this process to occur.

Figure 3 shows a schematic of a small Ag-Co cluster, where the dark atoms are Co and the white ones are Ag. (Though the details of the nucleation process cannot be extracted from our data, at some point of island formation a mixed cluster of Ag and Co must form.) The  $x$  axis marks the position along a closed-packed edge of the cluster. We have chosen this orientation for two reasons. First, the data show that the veins run along the root 3 direction, which means that the leading edges of the veins are close packed. Second, the growth of Co alone on the Ru(0001) substrate exhibits triangular islands indicating that three of the close-packed directions are preferred. Other experiments not discussed here [23] indicate that these step edge orientations are also those of the vein edges. Plotted along the  $y$  axis of Fig. 3 is the binding energy experienced by a Co atom along the edge. The closed-packed nature of the edge leads to small corrugations in the potential, consistent with fast edge diffusion as observed in the single metal phases. However, a step in the energy must occur at the interface since the energy of the Co atom increases as it crosses the interface. This step size  $\delta$  is approximately the chemical energy difference between a Co-Co bond and a Co-Ag bond. Thus, it is more difficult for Co to diffuse onto the Ag veins in order to terminate them. A similar diagram also exists for an Ag adatom, except that the energy barrier would be inverted relative to the diagram for Co (Fig. 3). The bonding of Ag to the edge of the Co vein would lead to a higher energy than for Ag-Ag bonding, again resulting in an additional diffusion barrier for Ag across interface edges. In this way, these energetics

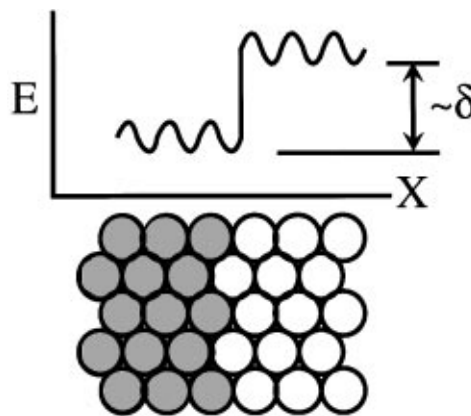


FIG. 3. Schematic of the energy diagram experienced by a Co at the edge of a vein structure. Ag and Co atoms are represented as white and black balls, respectively.

favor the continued growth of like-metal species in the observed vein structure. Furthermore, this simple model also explains the observed connection between the vein structure and the dendritic growth. At low temperature (below 170 °C) atoms diffusing along the edge are either reflected or desorbed at the barrier, reducing its effective diffusion length along the island edge. This would then naturally lead to dendritic growth and predict that both the veins and the dendritic growth should relax together as the thermal energy of the edge atoms overrides the interface energy, which is precisely what is observed experimentally (Fig. 2). These studies will be applied to a more extensive investigation of the link between the length scales of the veins and the dendritic growth. Details of the chemically induced edge diffusion barrier could conceivably be extracted [5].

In conclusion, we have observed that, in the growth of alloys at surfaces, the differing energetics of multicomponent films can drastically change the kinetics from the growth of the individual elements. One generic way this occurs is through edge diffusion barriers imposed by the relative binding energies of the components. This type of diffusion barrier will always exist in multicomponent growth systems due to the differing chemical bonding energies of the various species. Therefore 2D alloys are much more likely to exhibit dendritic growth as is exemplified by Ag-Co on Ru(0001).

We are grateful to Dr. G. S. Bales, Dr. N. C. Bartelt, Dr. J. C. Hamilton, and Dr. A. K. Schmid for many fruitful discussions and the reading of this manuscript. This work was supported by the Office of Basic Energy Science, Division of Materials Science, of the U.S. Department of Energy under Contract No. DE-AC04-94AL85000.

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