Irreversible processes of spontaneous whisker growth in bimetallic Cu-Sn thin-film reactions

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Using the thermodynamics of irreversible processes, we examine spontaneous interfacial reaction at room temperature in bimetallic Cu-Sn thin films. The reaction forms an intermetallic compound and is interfacial reaction limited. The volume change in forming the compound produces a biaxial compressive stress in the Sn film. The stress results in the growth of Sn whiskers to accompany the reaction. This is a case of an irreversible process of involving the interaction of chemical affinity and mechanical stress. However, the atomic mobility can significantly affect the reaction product and morphology. If the reaction temperature is raised above 100 °C, the compound formation becomes so fast that there is no time to grow whiskers, instead hillocks form. To model the whisker growth (or hillock growth), we assume that whiskers grow at weaker spots on the Sn surface where the surface oxide has been broken. These spots become localized stress relief centers, and they are surrounded by a long-range stress gradient needed for whisker growth.

I. INTRODUCTION

Under stress, thin films tend to relax and often the relaxation is accompanied by surface relief processes such as void formation of hillock and whisker growth. Surface relief phenomena have been the subjects of scientific and technical interest.[1-7] The mechanical strength of tin whiskers has been shown by Herring and Galt[1] to be near the theoretical limit. Whisker technology is important for high-strength composite materials.[3] Hillock growth on Pb films was found to be detrimental to Josephson devices.[4,5] Stress-induced void formation in conducting thin-film lines is currently a serious reliability issue in microelectronics.[6,7] These surface relief processes involve long-range atomic diffusion and require the interplay between stress and diffusion.

Stresses in thin films are affected by their substrates in several ways. We can bend the substrate to transmit the mechanical stress to the film. We can heat-treat them and allow thermal mismatch to produce the thermal stress. Chemical reactions, such as the formation of a silicide between a Ni film deposited on a Si substrate, can induce stresses due to volume change in the reaction.

Clearly, atomic diffusion in a solid can be driven by chemical affinity, as in solid-state reactions, or by stresses, as in creep and whisker growth. We ask whether these two forces interfere with each other or not. In the literature, most papers on chemical reactions in thin films have ignored the effect of stresses. The assumption is that the elastic strain energy (about 10^{-4} to 10^{-5} eV/atom) is much smaller than the chemical energy of forming intermetallic compounds (about 0.1 to 1 eV/atom). Nevertheless, whether or not this assumption alone is enough to ignore the interaction between chemical and mechanical driving forces is unclear.

It is well known that the thermodynamics of irreversible processes can be used to analyze the consequences of two interacting forces.[8,9] Yet the basic question of how to decide whether any two forces will interact or not is seldom addressed. A known criterion is that the forces must be additive; we should not add a scalar and a vector. Also, the fluxes must have a linear relation with the driving forces, i.e., we use linear equations. Still, we may need to consider other factors.

We consider a metal-to-semiconductor contact, e.g., the deposition of a Ni film on a Si wafer at liquid-nitrogen temperature. Electrical equilibrium is established immediately by charge transfer between the Ni and the Si, and a Schottky barrier is formed. however, chemical equilibrium between the Ni and the Si is not achieved. It requires the formation of $NiSi_2$ which does not occur at liquid-nitrogen temperature nor at room temperature. In this case the ions in the depletion layer have a negligible mobility, so the compound formation cannot occur. Hence, in addition to driving forces, the corresponding mobilities of the species must be considered.

In this paper we analyze the Cu-Sn thin-film reaction to illustrate the effect of mobility in irreversible processes. It has been shown that Cu reacts spontaneously with Sn at room temperature and the reaction is accompanied by the growth of Sn whiskers.[10] Since the whisker growth is driven by a compressive stress, this is a case of interaction between chemical affinity and mechanical stress. If we raise the temperature to above 100 °C, the kinetics of the reaction becomes so fast that it finishes in minutes so that there is no time for whisker to grow; instead, hillock growth is observed.[11] We find that the driving forces of mechanical stress and chemical affinity remain roughly the same, the outcome is altered by the kinetics of the reaction.

II. REVIEW OF THE INTERFACIAL REACTION IN BIMETALLIC Cu-Sn THIN FILMS

We shall briefly review the experimental findings of the reactions in Cu-Sn bimetallic thin films.[10,11] The films were deposited consecutively—first Cu by *e*-beam heating and then Sn by resistance heating—in a vacuum of

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10^{-7} Torr onto 1-in-diam fused quartz substrates kept at room temperature during deposition. The thicknesses of the Cu film and the Sn films were varied from 0.2 to 0.6 μm and from 0.4 to 2.5 μm, respectively.

Annealing at room temperature was carried out by keeping the samples in ambient in an air-conditioned room for up to one year. Grazing-incidence x-ray diffraction showed the formation of the compound η'-Cu_6Sn_5 at room temperature. The Sn film was stressed and the strain was about -0.16%, which is near the elastic strain limit. It was a biaxial compressive stress of about 0.7×10^9 dyne/cm^2. Whisker growth on the Sn surface was observed by scanning electron microscopy. The density of whiskers was about 10^3 to 10^4 whiskers/cm^2. The spacing between them was about hundreds of micrometers. The average growth rate of whiskers was about 0.2×10^{-8} cm/sec, and the typical length of a whisker was about a few tenths of a millimeter. For comparison, a single layer of Sn films was deposited and kept at room temperature on fused quartz substrates, but no whisker growth was observed.

Annealing in the temperature range of 60 °C to 150 °C was performed in a He furnace over periods of minutes to hours. Before and after annealing, the samples were examined by x-ray diffraction for stresses and phase changes and by Rutherford backscattering spectrometry for the kinetics of compound formation. It was found that below 60 °C, only Cu_6Sn_5 formed and it was a linear growth rate about 5 nm per day at room temperature. No activation energy of the growth of Cu_6Sn_5 was measured. During the growth of Cu_6Sn_5, the dominant diffusing species was determined to be Cu by using W markers. Above 80 °C, both Cu_3Sn and Cu_6Sn_5 formed. Hillocks rather than whiskers were observed at high-temperature annealing.

Figure 1 shows a schematic diagram of a cross section of the Cu-Sn reaction at room temperature, forming a layer of Cu_6Sn_5 intermetallic compound between the metals and growing a whisker on top of the Sn.[12] At room temperature, we can assume that there is no diffusion of Sn into Cu since Sn diffuses substitutionally in Cu and the diffusivity is negligible.[13] Hence, during the room-temperature formation of Cu_6Sn_5, we consider diffusion only in the compound and in the Sn. The Cu film serves as a source of Cu atoms for the reaction; then under the driving force of compound formation, Cu atoms depart from the Cu film and diffuse across the compound to react with Sn. Marker analysis indicated that the compound forms by the transport of Cu atoms across the compound, so the reaction between Cu and Sn occurs at the Cu_6Sn_5/Sn interface. The dominant flux in the compound is Cu, as indicated by the arrow in the compound in Fig. 2.

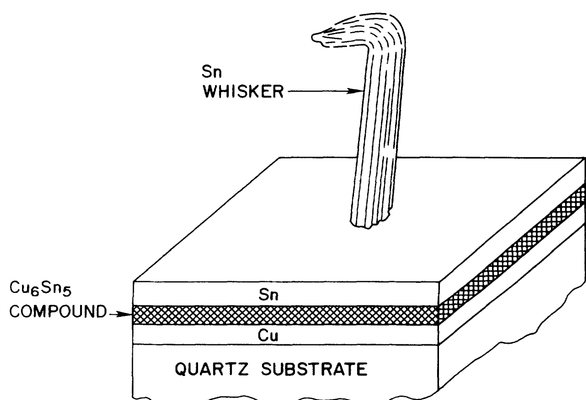

FIG. 1. A sketch of a Sn whisker grown on top of the bimetallic Cu-Sn thin films reacted at room temperature forming the Cu_6Sn_5 compound.

If the Sn surface is assumed to be free of oxide, the surface becomes an effective source and sink of vacancies. Because the Sn was measured to be under a biaxial compressive stress and since its surface is free of normal stresses, there exists a vacancy concentration gradient across the Sn layer on the basis of the Nobarro-Herring model of point defect formation in a stressed solid.[14] Specifically, there is a flux of vacancies going from the free surface of Sn towards the Cu_6Sn_5/Sn interface. At the same time, a counter flux of Sn atoms (mainly via grain boundaries intersecting the free surface) goes to the free surface in order to release the compressive stress. Again, the flux is depicted by the arrow in the Sn layer. If we further assume that the compound formation is rather uniform over the entire interface, we therefore expect no long-range lateral diffusion in the sample and in turn no whisker growth. Here the lateral-diffusion distance of the Sn atoms is only about the average radius of a grain in the Sn film. It has been observed that a polycrystalline Al thin film deposited and stressed compressively in ultrahigh vacuum forms no hillocks.[15]

In an ambient environment, the Sn surface forms an oxide which is known to be very stable and protective. In this case, we assume then that the oxidized surface of Sn is no longer a good source and sink of vacancies. When such an oxidized film is subjected to a compressive stress, the Nabarro-Herring model of detect formation does not operate effectively. In other words, vacancy sources become inadequate in maintaining a gradient of vacancies across the film. The film will be stressed rather uniformly.

To release the stress in such a film, we invoke a localized model, in which we assume that the oxide at certain spots of the Sn surface is broken, so that stress is released at these spots. Whiskers then grow on them. In Fig. 3, for example, a schematic diagram shows a whisker grow-

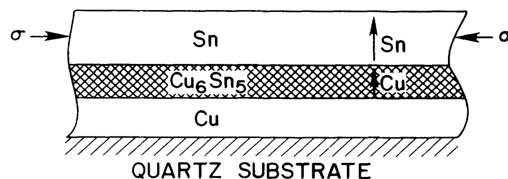

FIG. 2. A sketch of the cross section of the bimetallic Cu-Sn thin films forming the compound Cu_6Sn_5. The surface of Sn is assumed to be free of oxide. The arrows indicate the fluxes in the Sn and the compound.

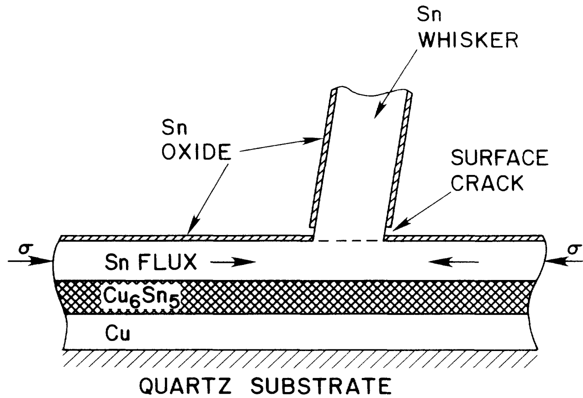

FIG. 3. A sketch of the cross section of the bimetallic Cu-Sn thin films forming the compound Cu_6Sn_5 and a whisker. The surfaces of the Sn and the whisker are oxidized except the base of the whisker where the oxide is broken. A lateral flux of Sn is indicated by arrows in the Sn film.

ing out of the Sn film surface. At the base of the whisker, represented by the dotted line, it is unstressed. As we have assumed, the surface oxide around the base is broken, i.e., there is a surface crack. The crack exposes the native surface of Sn where vacancies can be generated. Because the growth of a whisker occurs at the base, the crack cannot be healed, so it can serve continuously as a vacancy source. The flow of vacancies from the crack leads to two vacancy gradients: one is normal to, and another one parallel to, the film surface. The counterflow of Sn atoms, as indicated by the arrows in Fig. 3, provides the long-range mass transport needed for whisker growth.

As long as the stress in the Sn is maintained by the chemical reaction, a spontaneous growth of whiskers is sustained. We shall discuss the rate of whisker growth and the rate of chemical reaction later. We note that the growth of a whisker is assumed to occur at the base rather than at the tip of the whisker. One reason to rule out the growth at the top is that it requires a diffusional distance which is too long to be reasonable. Besides, the morphology of the tip remains unchanged during whisker growth; the observation supports a base growth.

III. THE DRIVING FORCE OF INTERFACIAL-REACTION-LIMITED PROCESSES

Since the growth rate of Cu_6Sn_5 is linear, we consider the reaction at the Cu_6Sn_5/Sn interface to be interfacial reaction limited. To obtain the driving force for the reaction in a closed system, we define the chemical affinity A_r of any one of the reactions r such that[8,9]

$$\sum_r A_r d\xi_r = \sum_k \mu_k dn_k \ , \tag{1}$$

where

$$dn_k = \sum_r \nu_{kr} d\xi_r \tag{2}$$

and

$$A_r = -\sum_k \nu_{kr}\mu_k \ , \tag{3}$$

where ν_{kr} is the stoichiometric number of species k in the chemical reaction r, ξ_r is the extent of the reaction and is a reaction variable, μ_k is chemical potential of species k, and n_k is the amount of species k in the reaction.

When there is only one chemical reaction such as

$$6\mathrm{Cu}+5\mathrm{Sn}\rightarrow \mathrm{Cu_6Sn_5} \ , \tag{4}$$

we have the chemical affinity

$$A = -\sum_k \nu_k\mu_k = \mu_\eta - 6\mu_{\mathrm{Cu}} - 5\mu_{\mathrm{Sn}} \ , \tag{5}$$

where μ_η is the chemical potential of the Cu_6Sn_5 compound molecule and μ_{Cu} and μ_{Sn} are the chemical potentials of the unreacted Cu and Sn, respectively. The Gibbs free-energy change of the reaction is

$$dG = -S\,dT + V\,dp - A\,d\xi \ , \tag{6}$$

where S, T, V, and p have the usual meaning in thermodynamics. At constant temperature T and constant pressure p, the chemical driving force of the reaction is

$$X_1 = -\left.\frac{dG}{dy}\right|_{T,p} = A\frac{d\xi}{dy} \ . \tag{7}$$

The force is constant for the interfacial-reaction-limited reaction. It means that the slope of ξ with respect to y is constant. In other words, the force is independent of the position or coordinate of the reaction. Hence, the reaction rate is constant as the Cu_6Sn_5/Sn interface advances along the y axis, and the growth is linear.

For the mechanical force, the gradient of the chemical potential in the Sn under stress in cylindrical coordinates as shown in Fig. 4 is[14]

$$X_r = -\frac{\partial\sigma\Omega}{\partial r} \ , \tag{8}$$

where σ and Ω are the stress and atomic volume (or partial molar volume in a binary system), respectively. The mechanical driving force will be used in Sec. IV to calculate the rate of whisker growth.

IV. A MODEL OF Sn WHISKER GROWTH AND ITS GROWTH RATE

To consider the growth of a whisker, we assume that the whiskers have a diameter of $2a$ and a separation of $2b$ and they have a steady-state growth in a diffusional field which can be described by a two-dimensional continuity equation in cylindrical coordinates as represented by Fig. 4:

$$\nabla^2\sigma = \frac{\partial^2\sigma}{\partial r^2} + \frac{1}{r}\frac{\partial\sigma}{\partial r} = 0 \ . \tag{9}$$

The boundary conditions are

$$\sigma = \sigma_0 \quad \text{at } r = b$$

$$\sigma = 0 \quad \text{at } r = a \ .$$

The solution is

$$\sigma = B\sigma_0 \ln\frac{r}{a} \ ,. \tag{10}$$

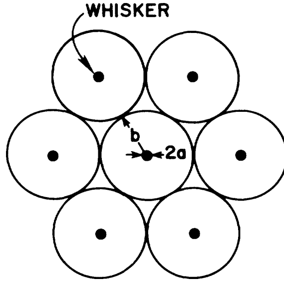

FIG. 4. A sketch of the top view of regularly spaced whiskers on the Sn surface. The whiskers have a diameter of $2a$ and a spacing of $2b$.

where $B=[\ln(b/a)]^{-1}$ and σ_0 is the stress in the Sn film due to the chemical reaction. It is assumed that σ_0 is constant because the stress is sustained by the reaction, and it decays only when the reaction is over. Knowing Eq. (10), we can evaluate the driving force:

$$X_r=-\frac{\partial\sigma\Omega}{\partial r} . \tag{8}$$

Then the flux to grow the whisker is evaluated at $r=a$ to be

$$J=C\frac{D}{kT}X_r=\frac{B\sigma_0 D}{kTa} . \tag{11}$$

We note that in a pure metal, $C=1/\Omega$. The volume of material transported to the base of the whisker in a period of Δt is

$$JA\,\Delta t\,\Omega=\pi a^2\Delta h , \tag{12}$$

where $A=2\pi as$ is the peripheral area of the growth step at the base, s is the step height, and Δh is the increment of length of the whisker in Δt. The growth rate of the whisker is

$$\frac{\Delta h}{\Delta t}=\frac{JA\Omega}{\pi a^2}=B\frac{\sigma_0 D}{kTa}\frac{2\pi as\Omega}{\pi a^2}=\frac{2}{\ln(b/a)}\frac{\sigma_0\Omega sD}{kTa^2} . \tag{13}$$

To evaluate the whisker growth rate given by Eq. (13), we take the measured data[10,11] roughly to be $a=3$ μm, $b=0.1$ mm, $\sigma_0\Omega=0.01$ eV (at $\sigma_0=0.7\times10^9$ dyne/cm^2), $kT=0.025$ eV at room temperature, $s=0.3$ nm, and $D=10^{-8}$ cm^2/sec (the self-grain-boundary diffusivity of Sn at room temperature), we obtain a growth rate about 0.1×10^{-8} cm/sec. At this growth rate, we expect a whisker of 0.3 mm after one year, which agrees well in order of magnitude with the observed whisker length. Experimentally, it was measured that whiskers have an average growth rate of about 0.2×10^{-8} cm/sec. The agreement between the calculated and the measured is quite reasonable; nevertheless, some of the discrepancy may come from the uncertainty in diffusivity. Since there is no direct measurement of self-grain-boundary diffusion of Sn, we can only estimate the grain-boundary diffusivity from the published self-lattice diffusion in Sn, which will be discussed in Sec. V.

V. EFFECT OF THE RATE OF COMPOUND FORMATION ON WHISKER GROWTH

The spontaneous growth rate of Cu_6Sn_5 at room temperature was measured to be linear and about 5 nm per day. At this rate, a Sn film of 500 nm will be consumed in about 200 days. This is the typical period of whisker growth and we recall that the room-temperature reaction was kept to one year. On the other hand, when we raised the temperature to 150 °C, the reaction rate was so fast that a 500-nm Sn film was reacted in 15 min forming a Cu_3Si compound.[11] The ratio of reaction times between the two (at room temperature and at 150 °C) is 10^4 to 10^5. This difference prevents whiskers from growing at high temperature.

Since whisker growth requires a long-range diffusion, the atomic transport obeys the relation of $x^2=4Dt$, where x is the lateral-diffusion distance of Sn atoms and the constant "4" is chosen arbitrarily for the purpose of estimating the effective diffusivity D. If we assume that the distance of diffusion (the spacing between whiskers) remains the same, the effective diffusivity at high temperature must be increased by four to five orders of magnitude in order to keep the product Dt constant since the time has been reduced from 200 days to 15 min. We will show that it is not possible to increase the diffusivity by so much in the present case.

The metallic Sn has a body-centered tetragonal crystal structure. Its self-lattice diffusivities in the directions parallel and normal to the c axis are slightly different; they are, respectively,[16,17]

$$\begin{aligned} D_{\parallel}&=7.7\times\exp(-25.6\ \text{kcal/RT}) ,\\ D_{\perp}&=10.7\times\exp(-25.2\ \text{kcal/RT}) . \end{aligned} \tag{14}$$

The lattice diffusivities are too slow to be responsible for whisker growth at room temperature. Self-grain-boundary diffusion of Sn has not been determined. If we assume that the large-angle grain-boundary diffusion requires about one-half of the activation energy of lattice diffusion given in Eq. (14), we estimate an increase of only two orders of magnitude (not four to five orders of magnitude as required) of the diffusivity at room temperature to that at 150 °C. Hence, the grain-boundary diffusivity at 150 °C is not fast enough to grow whiskers in a period of 15 min.

Now if we decrease the whisker spacing by one order of magnitude, the grain-boundary diffusivity at 150 °C becomes sufficient. However, we have increased the density (the number of whiskers per unit area) by two orders of magnitude. In such a case we have hillocks rather than whiskers because of mass conservation. In general, we find that the height of a hillock is about two orders of magnitude shorter than that of a whisker. Experimentally, Sn whiskers have a height of about several hundred microns,[10] while Sn hillocks have a height of about a few microns.[11]

To calculate the hillock growth, we again use Eq. (13) and take $a=3$ μm, $b=0.01$ mm (which is one order of magnitude smaller than that used in calculating whisker growth in Sec. IV), $\sigma_0\Omega=0.01$ eV, $kT=0.0365$ eV at 150 °C, $s=0.3$ nm, and $D=2\times10^{-6}$ cm^2/sec (the self-

grain-boundary diffusivity of Sn at 150 °C). We obtain a growth rate about 0.3×10^{-6} cm/sec. At this growth rate, we have a growth of 2.7 μm after 15 min, which is the height of a hillock rather than a whisker. Therefore, whiskers are absent in the high-temperature reaction.

In the above calculation, we note that if we increase the distance "*b*," we will have a slower growth rate, as shown by Eq. (13). Also, we have taken the stress σ_0 to be constant since we assume that it is sustained by the reaction. But we have ignored the effect of thermal stress: the bimetallic thin films were deposited at room temperature, and annealed at 150 °C. Since the thermal stress would decay with the relaxation time, it becomes a nonsteady-state problem as has been presented in the literature.[4] By taking σ_0 to be constant and near the elastic limit, we have calculated the upper bound of the growth rate in the high-temperature reaction. Since it has already shown the absence of whiskers, a slower growth rate will not lead to whisker growth.

VI. DISCUSSIONS

In Sec. V we discussed the effect of atomic mobility on irreversible processes. We showed that at a high temperature (150 °C) the interfacial reaction between Cu and Sn is so fast that there is not enough time to grow whiskers. Instead, hillocks grow. However, we must also consider the effect of surface oxide on surface relief phenomena. Without a surface oxide, we expect no whiskers. There may be some small hillocks due to local microstructural inhomogeneity. With a thick surface oxide, we have proposed that surface cracks are required in order to grow whiskers. It is similar to the extrusion of a wire under high pressure except that in whisker growth it occurs by atomic diffusion rather than mechanical flow. When the surface oxide is very thin and can be broken easily by stresses or when the reaction occurs at a high temperature where the thermal stress plays the role of breaking the oxide easily, a high density of hillocks rather than whiskers will grow. Therefore, surface relief phenomena have a dependence on the driving force, atomic mobility, as well as the source and sink of point defects which monitor atomic mobility. With the same driving forces, a change in relative mobilities can alter the outcome of interference.

We have used the same equation (13) to describe the growth of both whiskers and hillocks. We make no effort to distinguish them except their morphology. Besides density (number per unit area), the duration of growth is different. However, the detailed atomic mechanism of growth may not be the same.

A specific assumption in whisker growth made in the above is the existence of a crack in the base of the whisker. While there was no attempt to observe such a crack, it is a very reasonable assumption. Otherwise, the surfaces of the Sn and the whisker are completely confined by the oxide. Often it has been observed that whiskers are bent, as shown in the sketch in Fig. 1. The bend can be explained if one part of the crack became healed during the growth and caused a slower growth in that part. The bend ceases when the crack is reopened by a buildup of stresses due to the asymmetrical growth.

VII. CONCLUSIONS

(1) We have analyzed the spontaneous interfacial reaction in bimetallic Cu-Sn thin films accompanied by Sn whisker growth. The fluxes of Cu and Sn are driven simultaneously by forces of chemical affinity and mechanical stress.

(2) We show that atomic mobility can change the outcome of the irreversible processes. When the reaction temperature of Cu and Sn is raised to 150 °C, hillocks rather than whiskers grow.

(3) Surface oxide on the Sn film plays a dominant role in affecting stress relaxation. Without the surface oxide, a homogeneous relaxation occurs over the entire film, so there is no long-range diffusion for whisker growth. With a thick and protective oxide, an inhomogeneous relaxation occurs at certain weak spots on the Sn surface where the oxide has been broken and whiskers grow upon them.

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