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Critical misfit of epitaxial growth metallic thin films①

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Abstract: The critical misfit of epitaxial growth metallic thin films f_c was thermodynamically considered. It is found that there exists a competition between the energy of the misfit dislocation of film and non-coherent interface energy of film-substrate. Equilibrium between these energies was present at a critical atomic misfit f_c. When the atomic misfit is larger than the critical value, epitaxial growth does not occur. The critical misfit of the epitaxial growth thin films can be predicted. The results show that f_c is proportional to the non-coherent interface energy of the film-substrate, and inversely proportional to the elastic modulus and the thickness of the film.

Key words: epitaxial growth film; atomic misfit; dislocation; interface energy
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1 INTRODUCTION

Thin metallic films epitaxially grown on metallic substrates have been the subjects of many studies because they present very unusual chemical, electronic and magnetic properties, which differ from the corresponding bulk counterparts[1, 2]. However, the film and the substrate generally have different lattice parameters. As a result, the lattice mismatch exists at the film/substrate interface and internal stresses are induced in the system. The epitaxial growth model is affected by the corresponding strain energy induced by the atomic misfit of film-substrate. When an epitaxial growth thin film is deposited onto a substrate that has a different lattice parameter than that of the film, the lattice misfit can be accommodated in two ways: the film can be elastically strained in order to bring it into registry with the substrate and/or the misfit can be accommodated by misfit dislocations within the film-substrate interface.

The concept of a limiting misfit as the upper limit of misfit below which epitaxial growth may occur was introduced by Royer, which motivated Franck and Merwe[3] to introduce the relevant concepts of misfit strain, misfit dislocations, critical misfit and critical thickness. The critical misfit f_c is homogeneously strained into registry with the substrate, and the critical thickness is the critical layer thickness above which an interface of given natural misfit loses registry by the introduction of misfit dislocations. The critical misfit and the thickness of the epitaxial growth films before misfit dislocations appear were predicted by many researchers[4-7]. However, misfit dislocations occur practically in most epitaxial growth films. With strain increasing, the energy of the film increases, the strain in the film is relaxed by formation of the misfit dislocations. When the strain in the film is relaxed entirely by the misfit dislocations, the interface energy of the film-substrate is mainly the misfit dislocation energy. Once it reaches some value that it is larger than the non-coherent interface energy of film-substrate, the interface is completely non-coherent. Therefore, there must be the critical atomic misfit of the film-substrate f_c for epitaxial growth. When the misfit is larger than critical value f_c, epitaxial growth film cannot be obtained. In this contribution, f_c is calculated based on thermodynamics and dislocation theory.

2 MODEL

When the strain in the film is relaxed entirely by the formation of the dislocations, the strain energy disappears, its interface free energy is the energy of misfit dislocations. When the energy of film reaches the non-coherent interface energy, the interface becomes completely non-coherent. For an epitaxial growth film, the interface of the film and the substrate must be coherent or semi-coherent.

When the solid is isotropic, the atomic misfit of film $f = |h_f - h_s|$, where h_f and h_s are the atomic distances of the nearest neighbor of the film and substrate respectively.

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The non-coherent interface energy of the film U_{in} can be simply calculated by

$$U_{in} = \gamma_{ss} A_f \quad (1)$$

where γ_{ss} is the solid-solid interface energy, A_f is the area of the interface.

It is well known that a liquid may be regarded as a solid with such a high concentration of dislocation cores that these are in contact everywhere[8]. Based on this theory, γ_{ss} is considered to be twice of the solid-liquid interface energy γ_{sl} approximately[9], namely

$$\gamma_{ss} \approx 2\gamma_{sl} \quad (2)$$

Over 50 years ago, Turnbull and Cech[10, 11] observed that the interfacial free energies of a variety of metallic elements exhibited a linear correlation with the enthalpy of fusion, and proposed a famous empirical relationship as follows:

$$\gamma_{sl} = khH_m / V_m \quad (3)$$

where k is a constant, h denotes the atomic diameter, H_m is the melting enthalpy of crystals, V_m denotes the molar volume. The coefficient of k is considered to be between 0.32 and 0.45. This relationship provides an important empirical "rule-of-thumb" for estimating interfacial free energies, but lacks a compelling physical explanation[12].

γ_{sl} has been deduced by use of Gibbs-Thomson equation and our model for the size-dependent melting temperature as follows[13-15]:

$$\gamma_{sl} = 2hS_{vib}H_m / (3V_m R) \quad (4)$$

where R is the ideal gas constant, S_{vib} is the vibrational part of the overall melting entropy S_m. For metallic crystals, $S_{vib} \approx S_m = H_m / T_m$, and T_m is the bulk melting temperature[16]. The predicted γ_{sl} for different types of crystals, such as "true metals" Au, "meta metals" Pb, semiconductors Bi, ionic crystals ice and organic crystals benzene and naphthalene, are confirmed by available experimental results in the experimental error range[13]. It is obvious that when $k = 2S_m/3R$, Eqn. (3) equals to Eqn. (4), which suggests that both H_m and S_m affect the size of γ_{sl}. Thus, Turnbull's empirical equation is improved in our model.

Substituting Eqn. (4) into Eqn. (2) yields

$$\gamma_{ss} = 4hS_{vib}H_m / (3V_m R) \quad (5)$$

The solid-solid interface consists of different crystals, as a first order approximation, a mean value for γ_{sl} is taken:

$$\gamma_{ss} \approx 4\overline{h}\,\overline{S}_{vib}\overline{H}_m / (3\overline{V}_m R) \quad (6)$$

where $\overline{h}$, $\overline{S}_{vib}$, $\overline{H}_m$, and $\overline{V}_m$ are the mean values of corresponding amounts of the two halves. It can be found that this approximation is proper for bicrystals from Table 1 and Fig. 1.

The comparisons of the model predictions for γ_{ss} in terms of Eqn. (6) with other theoretical results γ'_{ss} calculated in terms of the embedded atom method(EAM) interaction potentials are shown in Table 1 and Fig. 1. Fig. 1 as well as Table 1 reveal a good quantitative agreement between our theory and other theoretical values for the interface energy. The free energy of the solid-solid interface depends on not only the melting enthalpy, but also the vibrational component of the overall melting entropy.

Table 1 Comparison of γ_{ss} by model prediction in terms of Eqn. (6) with other theoretical γ'_{ss}

Film	γ_{ss}/(J·m^{-2})	γ'_{ss}[17]/(J·m^{-2})
Cu/Mo	1.195 7	0.909 9
Cu/W	1.190 0	1.369 7
Ni/Mo	1.371 3	1.006 1
Ni/W	1.358 5	1.409 8
Cu/Ni	0.887 3	0.724 1
Mo/W	1.614 4	1.688 5

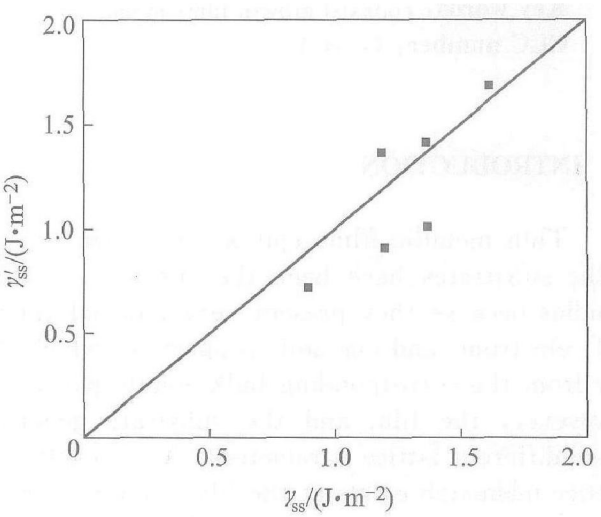

Fig. 1 Graph comparison of γ_{ss} by model prediction in terms of Eqn. (6) with other theoretical γ'_{ss}

The interface free energy of the fully relaxed film can be expressed as the sum of the misfit dislocation energy U_d induced by dislocation energy being equal to the product of misfit dislocation energy of a single dislocation(u_d) and the dislocation number(N) on the area of the interface of the film-substrate A_f. We have introduced the simplifying assumption that the film and substrate are elastically equivalent. It is assumed that dislocation is edge one that is parallel to x-axis or y-axis:

$$u_d = \frac{E_f b^2 l}{4\pi(1+\nu_f)(1-\nu_f)}\left[\ln\frac{\delta}{b} + 1\right] \quad [17]$$

where E_f and ν_f denote the elastic modulus and the Poisson's ratio of the film, l is the length of a dislocation. δ is an effective dislocation stress field radius, which is often approximated as the smaller of the film thickness t[16]. b is the Burgers vector, which is equal to the average atomic distance of the

nearest neighbor of the film and substrate. $N = A_f/(lD)$ with $D = b/f$ being the distance between two neighbor dislocations along x-axis or y-axis. Thus, the total number along two axes $N = 2N_i = 2fA_f/(l)$. Let $U_d = Nu_d$, then

$$U_d = \frac{E_f A_f \bar{h} f [\ln \frac{t}{\bar{h}} + 1]}{2\pi(1 - \nu_f^2)} \quad (7)$$

Let $U_d = U_{in}$ in terms of Eqns. (1) and (7) with a corresponding critical atomic misfit f_c where the interface transforms from a semi-coherent interface to a non-coherent interface due to the requirement of minimum of the interface energy. $U_d/U_{in} = (3\bar{V}_m R E_f f_c[\ln \frac{t}{\bar{h}} + 1])/[8\pi \bar{S}_{vib} \bar{H}_m (1 - \nu_f^2)]$, or

$$f_c = 8\pi \bar{S}_{vib} \bar{H}_m (1 - \nu_f^2)/(3\bar{V}_m R E_f)[\ln \frac{t}{\bar{h}} + 1] \approx \bar{S}_{vib} \bar{H}_m (1 - \nu_f^2)/\bar{V}_m E_f [\ln \frac{t}{\bar{h}} + 1] \quad (8)$$

3 RESULTS AND DISCUSSION

The above result implies that the film cannot grow epitaxially when f is larger than f_c. In light of Eqn. (8), f_c may shift to a larger value through increasing H_m value of substrate according to the definition of $\bar{H}_m$. The calculative results of maximal f_c by Eqn. (8) for some epitaxial growth thin films on different substrates are listed in Table 3, where the necessary parameters of Eqn. (8) are shown in Table 2, here the minimum value of the film thickness t is one atomic layer, i. e. $t/\bar{h} \approx 1$. The critical misfits in Table 3 show that other epitaxial growth films can be obtained, except Fe_{bcc}/Au(100) and Co/Pt(111) films. The results are approved by previous experiments. The above results show that the epitaxial growth film exactly depends on the energetic conditions. Moreover, as

Table 2 Needed parameters for calculation of Eqn. (8)

Element	h[18] / Å	V_m[19] / (cm^3 · mol^{-1})	T_m[19] / K	H_m[19] / (kJ · mol^{-1})	ν[20]	E[20] / GPa
Cu	2.556	7.1	1 357	13.05	0.343	129.8
Ni	2.492	6.59	1726	17.47	0.31	199.5
Pd	2.751	8.9	1 825	17.6	0.39	121
Pt	2.774	9.1	2 045	19.6	0.39	170
Ag	2.889	10.3	1 234	11.3	0.367	82.9
Co	2.497	6.7	1 768	16.19	0.32	211
Au	2.884	10.2	1 337	12.55	0.42	78.5
Mo	2.725	9.4	2 890	28.66	0.293	324.8
W	2.741	9.53	3 680	32.64	0.28	411
Fe(bcc)	2.483	7.1	1 809	13.8	0.293	211.4
Fe(fcc)	2.538[21]	7.03*	–	–	– 0.29*	200*

* $V_{m(fcc)Fe}$ is determined by $V_{m(bcc)Fe} - V_{m(fcc)Fe}/V_{m(bcc)Fe} = 0.01$[22], ν and E are substituted by those of austenite steel respectively.

Table 3 Calculative results of f_c by Eqn. (8)

Film	f	f_c	Film	f	f_c	Film	f	f_c
Ni/Pd(100)	0.095	0.102	Ag/Mn(100)	0.117	0.118	Cu/Mo(110)	0.066	0.166
Ni/Cu(100)	0.025	0.101	Cu/Pd(111)	0.071	0.105	Cu/W(110)	0.072	0.170
Mo/W(100)	0.006	0.085	Ni/Pt(111)	0.102	0.106	Ni/Mo(110)	0.093	0.132
Febcc/Au(100)	0.139	0.055	Co/Cu(111)	0.017	0.085	Ni/W(110)	0.099	0.134
Fefcc/Cu(100)	0.008	0.149	Co/Pt(111)	0.099	0.084	Nb/Febcc(110)	0.151	0.155
Fefcc/Ni(100)	0.018	0.093	Ag/Pt(111)	0.041	0.156			

mentioned above, a substrate with larger H_m value, and small thickness and elastic modulus of film will benefit obtaining an thin film by epitaxial growth.

4 CONCLUSIONS

In summary, through a thermodynamic considering, the critical atomic misfit of epitaxial growth thin film is determined by Eqn. (8). It is found that f_c is related with not only H_m value of the materials, but also the elastic modulus and the thickness of the film. f_c is proportional to the noncoherent interface energy of the film-substrate, and inversely proportional to the elastic modulus and the thickness of the film.

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