

CRITICAL THICKNESS OF EPITAXIAL GROWN SEMICONDUCTOR FILMS WITH STRAINED STRUCTURE

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The critical thickness of structural transition from a tetragonal structure to a normal bulk structure for epitaxial ultrathin films deposited on the metallic and semiconductor substrates is thermodynamically considered. It is found that equilibrium between the elastic energy of the tetrahedral structure and the film–substrate interface energy is present when a critical thickness is reached. The predictions of the critical thickness are in agreement with the experimental results of films.

Keywords: Epitaxial film; critical thickness; interface energy; semiconductor.

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1. Introduction

Both scientific and technological interests have contributed to rapid advances in the field of thin film epitaxy.^{1–3} One of the most intriguing questions in the field of crystal growth is which structure appears during the growth of a given semiconductor on a given substrate. The ability to grow good-quality epitaxial metal or semiconductor layer by various deposition methods is rather interesting scientifically.^{4–7} Some epitaxial metal or semiconductor thin films were successfully grown.^{5–15} A thermodynamically stable structure is dictated by the surface and interface free energies and by the difference in the lattice constant of the substrate and the material that is being deposited. The epitaxial growth leading to the structure of the grown films is affected by the corresponding substrate with certain crystal planes.⁸ It is clear that to minimize the total Gibbs free

energy of the film G , the film could prefer to take lattice strain at the film–substrate interface ε_i to avoid any increase of the film–substrate interface energy γ_i from a coherent interface to a semi-coherent or a noncoherent interface, since the γ_i value of the coherent interface is one order smaller than that of the noncoherent one. At some special cases, a metastable structure may be present, such as the high temperature phase of fcc Fe, since the structure has a smaller ε_i and thus γ_i . However, as the layer number n increases, or the surface (interface) area $A_f = V_f / (nh \sin \theta)$ decreases, where V_f is the volume of the film, $h \sin \theta$ shows layer distance of the film with h being the atomic diameter and θ the dihedral angle of the two layers, the total value of molar elastic energy U_{el} (and additional solid state transition enthalpy U_{ss} when the structure is a metastable one) will be larger than that of the molar interface

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energy U_i . Subsequently, the stable strain-free structure is recovered at n_c where a structural transition from the strained structure (and even from a metastable one) to a normal one occurs.

In this contribution, n_c of some semiconductor thin films is calculated based on classic elastic theory and an assumption that elastic strain on the free surface of the film is always absent even. The results show that the predictions for n_c are in agreement with the experimental results.^{13–15}

2. Model

For a film epitaxially grown on a substrate, G can be expressed as

$$G = g + U_{el} + U_s + U_i + U_{ss}, \quad (1)$$

where g denotes the bulk molar Gibbs free energy of the film, U_s the surface energy, U_{ss} the additional solid state transition enthalpy when the film has a metastable structure, which differs from the corresponding bulk one. Otherwise, $U_{ss} = 0$. To identify different terms, several subscripts are used: subscripts *ic*, *is*, and *in* denote the coherent interface, semi-coherent interface, and noncoherent interface; *f* and *s* the film and the substrate, respectively; 1 and 2 denote the states of a strained film with a coherent film–substrate interface and a strain-free film with a noncoherent or semi-coherent interface. Assuming that g and U_s values of the both structures are the same and $\gamma_{ic} \approx 0$ since it is one order smaller than γ_{in} and is only a fraction of γ_{is} , when the two structures are in equilibrium, $\Delta G = G_2 - G_1 = U_i - U_{el} - U_{ss} = 0$ at $n = n_c$, or,

$$U_i = U_{el} + U_{ss}. \quad (2)$$

Since U_i has two choices of U_{in} and U_{is} depending on the value of ε_i . U_{in} can be simply determined by

$$U_{in} = \gamma_{in} V_f / n h \sin \theta, \quad (3)$$

where γ_{in} has been determined by¹⁶

$$\gamma_{in} = 4h S_{vib} H_m / (3V_m R), \quad (4)$$

where S_{vib} is the vibrational part of the overall gram-atom melting entropy S_m , R is the ideal gas constant, V_m is the gram-atom volume, H_m is the gram-atom enthalpy of crystals. It is well known that S_m consists of at least three components: positional

S_{pos} , vibrational S_{vib} , and electronic S_{el} ,¹⁷

$$S_m = S_{vib} + S_{pos} + S_{el}. \quad (5)$$

Note that for metallic crystals, because S_{pos} and S_{el} are negligibly small, S_{vib} is determined approximately by¹⁸

$$S_{vib} \approx S_m \approx H_m / T_m, \quad (6)$$

where T_m is the bulk melting temperature.

However, for semiconductors and semi-metals, the melting is accompanied by the semiconductor-to-metal transition and S_{el} strongly contributes to S_m . In this situation, S_{vib} is determined by Mott's equation as $S_{vib} = 3R \ln(f_S/f_L) = (3/2)R \ln(\sigma_S/\sigma_L)$,¹⁹ where f and σ denote characteristic vibration frequency and electrical conductivity with subscripts of S and L for crystal and liquid, respectively.¹⁹ However, because the parameters in Eq. (6) are unavailable, the following equation can be utilized to simplify the calculation¹⁷

$$S_{vib} = S_m - R. \quad (7)$$

Since the interface in the considered case consists of the film and the substrate, as a first-order approximation, a mean value of them for γ_{in} is taken as

$$\gamma_{in} = (\gamma_{in-f} + \gamma_{in-s})/2 \approx 4\bar{h}\bar{S}_{vib}\bar{H}_m / (3\bar{V}_m R), \quad (8)$$

where \bar{h} , \bar{S}_{vib} , \bar{H}_m , and \bar{V}_m are the mean values of corresponding amounts of the film and the substrate.

U_{is} is induced by dislocation formation energy. Thus, this value is equal to the product of dislocation formation energy of a single dislocation (u_{is}) and the dislocation number on A_f (N) where A_f is the area of the film. Let x - and y -axes be horizontal directions along the interface, z -axis be perpendicular to the interface and the corresponding subscripts denote the axis direction, on the assumption that dislocations are edge dislocations, $u_{is} = \frac{E_f \bar{h}^2 l}{8\pi(1+\nu_f)(1-\nu_f)}$, where E_f is the Young modulus, ν_f denotes the Poisson ratio, l is the length of a dislocation, \bar{h} here has the same size of the Burgers vector.²⁰ $N_i = 2V_f / (lDn h \sin \theta)$ with $D = \bar{h}/\varepsilon_i$ being the distance between two neighbor dislocations along x - or y -axis. Thus, the total number along two axes $N = 2N_i = 4\varepsilon_i V_f / (l n \sin \theta \bar{h}^2)$ with $h \approx \bar{h}$ and V_f is the volume of the film. Let $U_{is} = Nu_{is}$, it reads

$$U_{is} = \frac{E_f V_f \varepsilon_i}{2\pi(1-\nu_f^2)n \sin \theta}. \quad (9)$$

U_{el} value in Eq. (2) can be determined based on the classic elastic theory. For an isotropic solid, it is

assumed that $\varepsilon_x = \varepsilon_y = 0$ at the surface of the film and $\sigma_z = 0$, where σ denotes the stress since ε_i does not induce σ_z ,

$$\varepsilon_x = \varepsilon_y = \varepsilon_i [1 - z/(nh \sin \theta)], \quad (10)$$

where z shows the distance from the interface along z -axis. ε_i in Eq. (10) is expressed as

$$\varepsilon_i = (h_f - h_s)/h_s. \quad (11)$$

According to Hooke's law, $u_{el} = \frac{E_f}{1-\nu_f} \varepsilon_i^2 [1 - z/(nh \sin \theta)]^2$, where u_{el} shows the unit volume elastic energy,

$$\begin{aligned} U_{el} &= \int_V u_{el} dV \\ &= \frac{A_f E_f \varepsilon_i^2}{1-\nu_f} \int_0^{nh \sin \theta} [1 - 2z/(nh \sin \theta) \\ &\quad + z^2/(nh \sin \theta)^2] dz, \end{aligned}$$

or

$$U_{el} = \frac{V_f E_f \varepsilon_i^2}{3(1-\nu_f)}. \quad (12)$$

When U_i determined by Eq. (3) or Eq. (9) and U_{el} in Eq. (12) are substituted into Eq. (2) at $n = n_c$,

$$n_c = \frac{4(1-\nu_f) \bar{S}_{vib} \bar{H}_m}{\sin \theta \bar{V}_m R E_f f(U_{ss}) \varepsilon_i^2}, \quad (13)$$

where

$$f(U_{ss}) = 1 + \frac{3(1-\nu_f) U_{ss}}{E_f \varepsilon_i^2 V_f}. \quad (14)$$

Note that when $U_{ss} = 0$, $f(U_{ss}) = 1$ in Eq. (13), which is the case without metastable phase. From Eq. (13), n_c is proportional to $1/\varepsilon_i^2$. Thus, as ε_i decreases, n_c increases.

3. Results and Discussion

To understand a general characteristic of the model prediction of Eq. (13), a 3D plot for the function of n_c vs U_i and ε_i in terms of Eq. (13) is shown in Fig. 1 where some assumed parameters are given. It is clear that a thicker epitaxial film can be obtained when ε_i value is small and U_i value or γ_i value is larger.

The detailed model predictions of Eq. (13) for n_c and the corresponding experimental results n'_c of some films grown epitaxially on different metallic and semiconductor substrates are listed in Table 2, where the necessary parameters used in Eq. (13) are shown

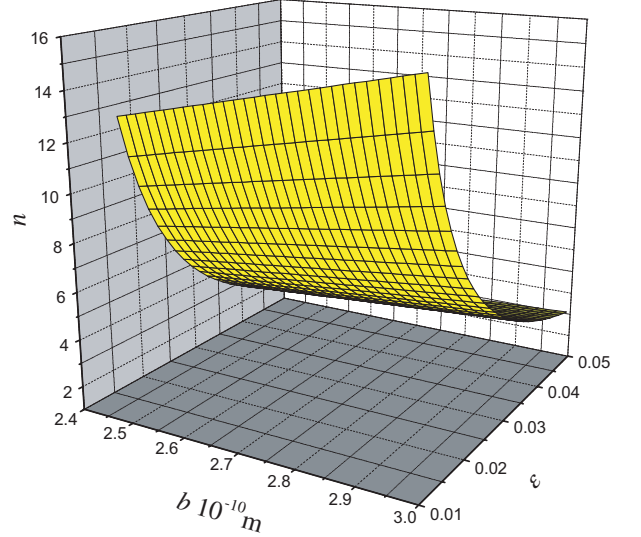


Fig. 1. A 3D plot for the function of n_c vs U_{in} and ε_i in terms of Eq. (13) where $h \sin \theta = 0.25$ nm, $E = 100$ GPa and $\nu = 0.3$ are taken.

Table 1. The needed parameters for the calculation of Eq. (13) where h is in Å, V_m in $\text{cm}^3/\text{g-atom}$, T_m in K, H_m in kJ/g-atom , S_{vib} in J/g-atom K , and E in GPa. $V_m = N_0 v_m$, where N_0 is the Avogadro's constant and v_m is the mean atom volume in the corresponding crystalline structure, $v_m = a^3/8$ for zinc blende structure. S_{vib} values are calculated by Eq. (7) for semiconductors. h_s of InAs, GaAs, and SiC are taken as the averaged covalent diameter of In ($h = 2.88$ Å) and As ($h = 2.4$ Å), Ga ($h = 2.52$ Å) and As ($h = 2.4$ Å), Si ($h = 2.22$ Å) and C ($h = 1.54$ Å), respectively.

Substance	h	V_m	H_m	T_m	S_{vib}
InAs	2.64^{21}	12.1^{22}	26.36^{17}	1215^{17}	17.54
GaAs	2.46^{21}	13.6^{22}	48.55^{17}	1511^{17}	27.97
SiC	1.88^{21}	6.2^{23}	8.75^{24}	3259^{24}	2.69

in Table 1. The predicted results are in agreement with the experimental ones.

The above agreements imply that the film-substrate may be semi-coherent or noncoherent, which exactly depends on the energetic conditions. As ε_i decreases, n_c increases. Owing to the requirement of lowering of the film-substrate interface energy, a film can even take a metastable structure with smaller mismatch on the interface. It is interesting that since now the metastable structure is energetically favorable, the structural transforms to the corresponding stable structure directly

Table 2. Comparison between model predictions of Eq. (13) (n_c) and experimental results (n'_c) for some semiconductor films, where Eqs. (13) and (14) are utilized according to the relative value of ε_i and whether there exists U_{ss} . $\sin\theta$ values in Eq. (13) are $\sqrt{2}/2$ and $\sqrt{6}/2$, respectively, for (100) and (0001) planes. ε_i is determined by Eq. (11) with data of Table 1.

Film/substrate(facet)	ε_i	n_c	n'_c
Fe _{bcc} on InAs(100)	0.25	1.2	3.5 ¹³
Fe _{bcc} on GaAs(001)	0.28	2	3 ¹⁴
Si on SiC(0001)	0.25	1.3	1.4 ¹⁵

without possibility to form the strained tetragonal structure. Moreover, as above-mentioned, a substrate with larger H_m value will benefit the obtainment of a larger n_c value.

4. Conclusion

In summary, through a thermodynamic consideration, the number of critical layers of epitaxial grown ultrathin films on metallic and semiconductor matrixes has been determined for several elements. It is found that the predicted values are in agreement with the experimental results where n_c is related to not only ε_i but also H_m . In order to obtain a larger n_c value, a smaller ε_i value and a larger H_m value are needed.

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