Thin Solid Films 583 (2015) 7–12

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Theoretical investigation of the thermodynamic properties of metallic thin films

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ARTICLE INFO

Article history:
Received 19 September 2014
Received in revised form 7 March 2015
Accepted 18 March 2015
Available online 27 March 2015

Keywords:
Metallic thin films
Thermodynamic properties
Specific heats
Anharmonicity
Statistical moment method

ABSTRACT

The thermodynamic properties of metallic thin films with face-centered cubic structure at ambient conditions were investigated using the statistical moment method including the anharmonicity effects of thermal lattice vibrations. The analytical expressions of Helmholtz free energy, lattice parameter, linear thermal expansion coefficient, specific heats at the constant volume and constant pressure were derived in terms of the power moments of the atomic displacements. Numerical calculations of thermodynamic properties have been performed for Au and Al thin films and compared with those of bulk metals. This research proposes that thermodynamic quantities of thin films approach the values of bulk when the thickness of thin film is about 70 nm.

1. Introduction

With attractive properties for technological and industrial applications [1–3], metallic thin film has generated enormous scientific interests in material sciences. The knowledge about the thermodynamic and mechanical properties of metallic thin film such as the stress, the elastic modulus, elastic constants and the coefficient of thermal expansion, is of great importance to determine the parameters for the stability and reliability of the manufactured devices.

A number of experimental and theoretical studies have been performed to determine thermo-mechanical properties of metal and nonmetal thin films [4–8]. Many methods such as X-ray diffraction [4], Raman spectroscopy [5], nanoindentation technique [6,7], Brillouin scattering [8] were used for measuring the thermodynamic properties or mechanical properties of crystalline thin films on the substrates (for example: thermal expansion coefficient [9–11], heat capacity [12], Young's modulus and Poisson ratio [13]). A few theoretical or experimental systematic studies were done to explain the thermo-mechanical properties of metallic free-standing thin films. In addition, the previous theoretical studies mostly focused on the properties of metallic thin film at low temperature, and temperature dependence of the thermodynamic quantities has not been studied in detail.

The main purpose of this article is to investigate the thermodynamic properties of metallic free-standing thin film with face-centered cubic (FCC) structure using the statistical moment method (SMM) in quantum statistical mechanics [14,15]. The major advantage of our approach is that the thermodynamic quantities are derived from the Helmholtz free energy, and the explicit expressions of the linear thermal lattice expansion coefficient, specific heats at constant volume C_V and constant pressure C_P are presented taking into account the anharmonicity effects of the thermal lattice vibrations. The influence of surface and size effects on the thermodynamic properties has also been concerned.

2. Theory

2.1. The anharmonic oscillations of metallic thin film

Let us consider a metal free standing thin film has n^* layers with the thickness d. We assume that the thin film consists of two atomic surface-layers, two next atomic surface-layers and $(n^* - 4)$ atomic internal-layers (see Fig. 1). N_{ng}, N_{ng1} and N_{tr} are respectively the number of atoms on surface-layers, next-surface-layers and internal-layers of this thin film. Then, the potential energy of the system can be written as

$$\begin{aligned} U &= U^{ng} + U^{ng1} + U^{tr} \\ &= \frac{N_{ng}}{2}\sum_i \varphi_{io}^{ng}\left(\left|r_{i,ng} + u_{i,ng}\right|\right) + \frac{N_{ng1}}{2}\sum_i \varphi_{io}^{ng1}\left(\left|r_{i,ng1} + u_{i,ng1}\right|\right) \\ &\quad + \frac{N_{tr}}{2}\sum_i \varphi_{io}^{tr}\left(\left|r_{i,tr} + u_{i,tr}\right|\right), \end{aligned} \tag{1}$$

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http://dx.doi.org/10.1016/j.tsf.2015.03.040
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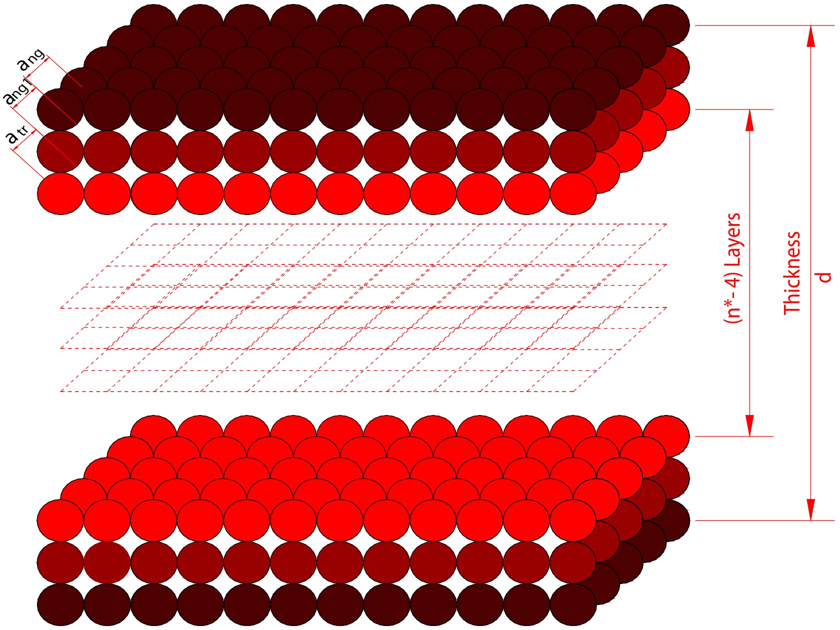

Fig. 1. The free-standing thin film.

where $U_0^{ng} = \frac{N_{ng}}{2}\sum_i \varphi_{i0}^{ng}\left(r_{i,ng}\right)$, $U_0^{ng1} = \frac{N_{ng1}}{2}\sum_i \varphi_{i0}^{ng1}\left(r_{i,ng1}\right)$ and $U_0^{tr} = \frac{N_{tr}}{2}\sum_i \varphi_{i0}^{tr}\left(r_{i,tr}\right)$ and r_i is the equilibrium position of *ith* atom, u_i is its displacement of the *ith* atom from the equilibrium position; φ_{i0}^{ng}, φ_{i0}^{ng1}, φ_{i0}^{tr} are the effective interatomic potential between 0^{th} and i^{th} surface-layer atoms, next-surface-layer atoms, internal-layer atoms, and U_0^{ng}, U_0^{ng1}, U_0^{tr} represent the sum of effective pair interaction energies for surface-layer atoms, next-surface-layer atoms and internal-layer atoms, respectively.

For surface-layer atoms of thin film, the atomic force acting on the given 0^{th} atom in the lattice can be evaluated by taking derivative of the internal energy of the ^{ith} atomic site and evaluating the power moments of the atomic displacements. If the 0^{th} surface-layer atom in the lattice is affected by a supplementary force p, then the total force acting on it must be equal to zero, and one gets the force balance relation as [14,15]

$$\sum_i \left(\frac{\partial^2 \varphi_{io}^{ng}}{\partial u_{i,ng}^2}\right)_{eq} \left\langle u_{i,ng}\right\rangle_p + \frac{1}{2}\sum_i \left(\frac{\partial^3 \varphi_{io}^{ng}}{\partial u_{i,ng}^3}\right)_{eq} \left\langle u_{i,ng}^2\right\rangle_p + \frac{1}{3!}\sum_i \left(\frac{\partial^4 \varphi_{io}^{ng}}{\partial u_{i,ng}^4}\right)_{eq} \left\langle u_{i,ng}^3\right\rangle_p - p = 0. \tag{2}$$

Using moment expansion formulas [14,15], one can find the thermal average displacements of the surface-layer atoms $\langle u_{i,ng}^2\rangle$ and $\langle u_{i,ng}^3\rangle$ (so-called the second-order and the third-order moments) in terms of the first moment $\langle u_{i,ng}\rangle$. Then Eq. (2) is transformed into the new differential equation as

$$\gamma_{ng}\theta^2 \frac{d^2 y_{ng}}{dp^2} + 3\gamma_{ng}\theta y_{ng}\frac{dy_{ng}}{dp} + \gamma_{ng} y_{ng}^3 + k_{ng} y_{ng} + \gamma_{ng}\frac{\theta}{k_{ng}}\left(x_{ng}\coth x_{ng} - 1\right) y_{ng} - p = 0, \tag{3}$$

where

$$y_{ng} \equiv \, < u_{i,ng} >_p; x_{ng} = \frac{\hbar\omega_{ng}}{2\theta}; \theta = k_B T, \tag{4}$$

$$k_{ng} = \frac{1}{2}\sum_i \left(\frac{\partial^2 \varphi_{io}^{tr}}{\partial u_{i\alpha}^2}\right)_{eq} \equiv m_0 \omega_{ng}^2, \tag{5}$$

$$\gamma_{1ng} = \frac{1}{48}\sum_i \left(\frac{\partial^4 \varphi_{io}^{ng}}{\partial u_{i\alpha}^4}\right)_{eq}, \tag{6}$$

$$\gamma_{2ng} = \frac{6}{48}\sum_i \left(\frac{\partial^4 \varphi_{io}^{ng}}{\partial u_{i\beta}^2 \partial u_{i\gamma}^2}\right)_{eq}, \tag{7}$$

$$\gamma_{ng} = \frac{1}{12}\sum_i \left[\left(\frac{\partial^4 \varphi_{io}^{ng}}{\partial u_{i\alpha}^4}\right)_{eq} + 6\left(\frac{\partial^4 \varphi_{io}^{ng}}{\partial u_{i\beta}^2 \partial u_{i\gamma}^2}\right)_{eq}\right] = 4\left(\gamma_{1ng} + \gamma_{2ng}\right), \tag{8}$$

and k_B is the Boltzmann constant, T is the absolute temperature, m_0 is the mass of atom, ω_{ng} is the frequency of lattice vibration of surface-layer atoms; k_{ng}, γ_{1ng}, γ_{2ng}, γ_{ng} are the parameters of crystal depending on the structure of crystal lattice and the interaction potential between atoms; $u_{i\alpha}$, $u_{i\beta}$, $u_{i\gamma}$ are the displacements of *ith* atom from equilibrium position on the direction $\alpha(\alpha = x, y, z)$, $\beta(\beta = x, y, z)$, $\gamma(\gamma = x, y, z)$, respectively, and the subscript *eq* indicates the evaluation at equilibrium.

For determining the displacement $< u_{i,ng} >$ of the surface-layer atom, the symmetry property which is appropriate for cubic crystals is used

$$< u_{i\alpha} > \, = \, < u_{i\gamma} > \, = \, < u_{i\eta} > \, = \, < u_{i,ng} >. \tag{9}$$

Then, the solutions of the nonlinear differential Eq. (3) can be expanded in the power series of the supplemental force p as

$$y_{ng} = y_0^{ng} + A_1^{ng} p + A_2^{ng} p^2. \tag{10}$$

Here, y_0^{ng} is the average atomic displacement in the limit of zero of supplemental force p. Substituting the above expression into the original differential Eq. (3), one can get the coupled equations on the coefficients A_1^{ng} and A_2^{ng}, from which the solution of y_0^{ng} is given as [14,15]

$$y_0^{ng} \approx \sqrt{\frac{2\gamma_{ng}\theta^2}{3k_{ng}^3} A_{ng}}, \tag{11}$$