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Internal stress analysis of electroplated films based on electron theory

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Abstract: Cu films on Fe, Ni and Ag substrates, Ni films on Fe and Ag substrates, Ag film on Cu substrate, Cr film on Fe substrate, Ag film on Ag substrate, Ni film on Ni substrate and Cu film on Cu substrate were deposited by electroplating. The average internal stress in all films, except Cr, was in-situ measured by the cantilever beam test. The interfacial stress is very large in the films with different materials with substrates and is zero in the films with the same material with substrates. The interfacial stress character obtained from the cantilever beam bending direction is consistent with that obtained from the modified Thomas–Fermi–Dirac electron theory.

Key words: metal film; deposition; interface; internal stress; electron density

1 Introduction

Internal stress in the films has a great influence on the performance and reliability of the film devices. Internal stress generation mechanism and measurement methods in thin films are of interest [1]. Internal stress in films can usually be divided into two components: thermal stress and intrinsic stress [2,3]. Thermal stress arises from the difference in the thermal expansion coefficients of film and the substrate materials [4]. Intrinsic stress is attributed to the cumulative effect of the flaws appearing in the film during deposition. Intrinsic stress mainly originates from the strained regions, both in the film, and at the film/substrate interface. Therefore, the intrinsic stress consists of the interfacial and the growth stresses. It is assumed that the interfacial stress derives from the lattice mismatch, voids and dislocations at the interface. When dealing with the interfacial stress, CHENG et al [5] were not concerned with the effects of the interfacial structure on the interfacial stress. Based on the modified Thomas−Fermi−Dirac (TFD) electron theory, they pointed out that the interfacial stress existed as a result of the continuous change of electron densities across the interface. Thus, understanding the relationship between the interfacial crystal structure and the electron density distribution at the interface is problematic.

TFD electron theory is based on the Fermi statistics for electrons inside the condensed materials under the Coulomb field, where the Pauli exclusion principle was introduced explicitly by exchange interaction. TFD electron theory was successfully applied to calculating the electron density distribution inside an atom, and was successfully applied in the equations of state at high pressure under explosion. However, TFD electron theory gave a poor description of condensed matters. This was mainly caused by the inappropriate treatment of the boundary conditions for electrons [6]. CHENG et al [5,6] and REN et al [7] modified TFD electron theory. The modified TFD electron theory is known as the Thomas−Fermi−Dirac−Cheng (TFDC) electron theory. TFDC electron theory proposed two important boundary conditions at the interface, namely, the electron densities

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and the chemical potentials must be continuous in accordance with the quantum principles. CHENG et al [5] pointed out that internal stress existed at the interface as a result of the condition that the electron densities are continuous across the interface. It is important to note that the electron density here is the electron density of atom at the Wingner–Seitz radius.

The main measurement methods of the film internal stress are substrate deformation tests, bulge test and X-ray diffraction methods [8−12]. Cantilever beam test is one of the widely used substrate deformation tests; it is simple and reliable, and can provide in-situ measurements.

In our previous literature [13], the interfacial stress character (tension or compression) only for the electrodeposited Cu film on Fe substrate was well explained based on the TFDC theory (the measured result is consistent with the theoretical judged result). Whether this is an isolated case, or whether the interfacial stress character for the other electrodeposited films also can be well explained, this needs further exploration. In this research, electroplating was employed to prepare Cu films on Fe, Ni and Ag substrates, Ni films on Fe and Ag substrates, Ag film on Cu substrate, Cr film on Fe substrate (the film with different materials with substrate, i.e., film/substrate system with different materials), Ag film on Ag substrate, Ni film on Ni substrate and Cu film on Cu substrate (the film with the same material with substrate, i.e. film/ substrate system with same material). During electroplating, the deflections of all the film and the substrate bi-layer cantilever beams, except Cr film and Fe substrate bi-layer cantilever beam, were measured in-situ. The average internal stresses in all the films, except Cr, were calculated from the measured beam deflections. Distribution of the internal stress in the films was investigated. The interfacial stress character (tensile or compressive stress) of all films was analyzed according to the experimental results and TFDC electron theory, comparing the two.

2 Experimental

Electroplating was employed to prepare Cu films on Fe, Ni and Ag substrates, Ni films on Fe and Ag substrates, Ag film on Cu substrate, Cr film on Fe substrate, Ag film on Ag substrate, Ni film on Ni substrate, and Cu film on Cu substrate. The purity of the substrate materials was over 99.9%. The substrates dimensions were 80 mm× 4 mm× 0.15 mm. In order to eliminate the residual stress and reduce crystal defects, the substrates were annealed. The substrates were treated with mechanical polishing, washing off oil by hot aqueous alkali and acetone, and then commercial tape was placed on the specific area of the substrate in order to prevent the area from being coated.

To electroplate relatively pure simple substance films and eliminate stress caused by additives, the additives were not used or were used as little as possible. The composition of electroplating solution for preparing Cu film is: $CuSO_4\cdot5H_2O$ (200 g/L), H_2SO_4 (60 mL/L) and HCl (1 mL/L); for Ag film: $AgNO_3$ (44 g/L), $Na_2S_2O_3\cdot5H_2O$ (220 g/L), $K_2S_2O_5$ (44 g/L), CH_3COONH_4 (30 g/L) and $NH_2CSNHNH_2$ (0.8 g/L); for Ni film: $NiSO_4\cdot7H_2O$ (150 g/L), NH_4Cl (15 g/L), H_3BO_3 (15 g/L) and $CH_3(CH_2)_{11}OSO_3Na$ (0.1 g/L); for Cr film: CrO_3 (250 g/L), H_2SO_4 (2.5 g/L) and CeO_2 (3 g/L). The electrodeposition parameters for preparing Cu, Ag, Ni and Cr films are shown in Table 1. Deposition rate was measured first, and then the film thickness was controlled by electroplating duration.

Table 1 Electroplating parameters for preparing Cu, Ag, Ni and Cr films

Film	pH	Current density/($mA\cdot cm^{-2}$)	Deposition rate/($nm\cdot s^{-1}$)	Deposition temperature/°C
Cu	3−4	10	1.6	20−25
Ag	5−6	2.5	3.5	20−25
Ni	3−5	5	2.5	20−25
Cr	1−2	100	−	45

The measurement method of the deflection of the film and substrate bi-layer cantilever beam is the same that of our previous literature [13]. One end of a substrate was clamped; its other end was free to move due to the film internal stress. The substrate was straight before electroplating. The electroplated surface of the substrate was activated by hydrofluoric acid before electroplating. The vertical distance from the free end of the film and substrate bi-layer cantilever beam to the reference axis was measured in-situ during electroplating. The vertical distance was defined as the deflection of the cantilever beam. Schematic diagram of the in-situ measurement is shown in Fig. 1. Because the thickness

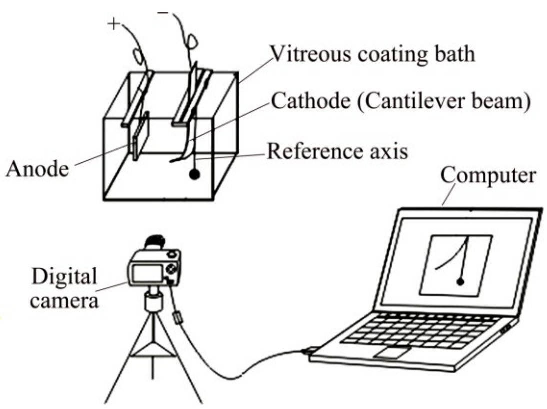

Fig. 1 Schematic illustration of in-situ internal stress measurement in films [13]

and the elastic modulus of the commercial tape are all very small, about 0.05 mm and 1.4 GPa, respectively, the influence of the commercial tape on the deflection of the film and substrate bi-layer cantilever beam can be neglected. The deflection values of the Cr film and Fe substrate bi-layer cantilever beam could not be measured because the electroplating solution of Cr film is opaque.

3 Theoretical considerations

3.1 Internal stress distribution in film

Internal stress in the film causes film/substrate composite to curve. When the film thickness is smaller compared with the thickness of the substrate, the average internal stress is given by [14]

$$\sigma = \frac{E_s t_s^2}{3(1-\upsilon_s^2)l^2} \cdot \frac{\delta}{t_f} \tag{1}$$

where σ is the average internal stress in the film, δ is the cantilever beam deflection, l is the cantilever beam length, E is the substrate elastic modulus, υ is the substrate Poisson ratio, and t is the film thickness. The subscripts s and f denote the substrate and the film, respectively.

When the cantilever beam bends towards the side of the film, the average internal stress in the film is tensile; when the cantilever beam bends towards the side of the substrate, the average internal stress in the film is compressive.

Stress in each layer is independent, thus when the film thickness is $t_{f(n)}$, correspondingly, the average internal stress is written as σ_n (n=1, 2, 3, ···). The average internal stress $\sigma_n^{(a)}$ in a thin layer between $t_{f(n-1)}$ and $t_{f(n)}$ (layer thickness $\Delta t_{f(n)}=t_{f(n)}-t_{f(n-1)}$) is given by [13]

$$\sigma_n^{(a)} = \frac{\sigma_n t_{f(n)} - \sigma_{n-1} t_{f(n-1)}}{t_{f(n)} - t_{f(n-1)}} \tag{2}$$

$\sigma_n^{(d)}$ is the internal stress (hereafter referred to as the distributed internal stress) at film thickness $t_{f(n)}^{(d)} = (t_{f(n)}+t_{f(n-1)})/2$. If $\Delta t_{f(n)}$ is very small, then $\sigma_n^{(d)}$ approximately equals $\sigma_n^{(a)}$, hence, $\sigma_n^{(d)}$ can be obtained using Eq. (2).

3.2 Interfacial stress character based on TFDC electron theory

Based on the TFDC electron theory, when a new phase grows on a surface of a parent phase, and the corresponding electron densities of their atomic surfaces are not equal, the crystal states near the interface must be changed to meet the continuity condition of the interface electron densities (i.e., near the interface, electron densities of the atomic surfaces become the same). The crystal state near the interface becomes different from the bulk. In order to achieve equal surface electron density of the atoms near the interface, atoms with high surface electron density on one side of the interface expand in volume, while atoms with low surface electron density on the other side of the interface shrink in volume. The expansion or shrinkage of the atoms causes the change of the inter-atomic distance (the lattice spacing). Consequently, the interfacial stress in the new phase and the parent phase is generated. Figure 2 shows the relationship between the inter-atomic distance and the inter-atomic force between atoms A_1 and A_2 of the new phase, or the parent phase near the interface. If atoms A_1 and A_2 have higher surface electron densities, the atomic volume should expand. The volume expansion will result in the increase of the inter-atomic distance from the equilibrium distance a_0 to a, so the internal force between atoms A_1 and A_2 is tensile. On the contrary, the inter-atomic distance on the other side of the interface should decrease, and the internal force is compressive. The inter-atomic distance gradually approaches the balance distance from the interface to the bulk.

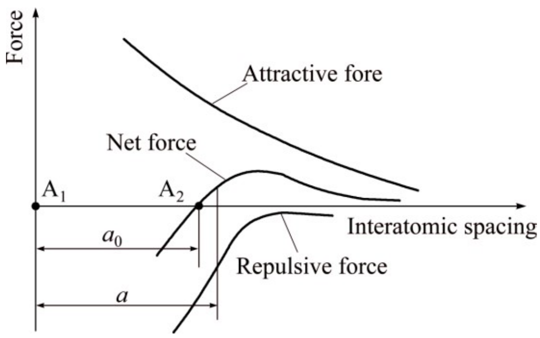

Fig. 2 Relationship between inter-atomic distance and inter-atomic force [15]

It should be stressed that TFDC electron theory is based on the Jellium (Wingner–Seitz) model. In this model atoms are not spherical atoms, and fill up the whole unit cell. Therefore, interface analyzed only based on the TFDC electron theory, such as the orientation relationship at interface, cannot be obtained.

Coherent and incoherent interfaces can be interpreted as follows: When the difference of the surface electron densities between the new phase atoms and the parent phase atoms is relatively small, the lattice spacing variation near the interface is also relatively small. Consequently, interfacial stress and interfacial strain energy are relatively small, thus dislocations and vacancies are not needed to reduce the strain energy. When the difference in the electron densities of the atomic surface is relatively large, the lattice spacing near the interface will change significantly. Dislocations and vacancies must be brought in to reduce the interfacial strain energy. When many dislocations and vacancies are brought to the interface between the new and parent phases, such that there is more than one dislocation for every four unit cells, coherent or semi-coherent interface cannot form. However, under this condition, the interfacial stress character can be deduced just from the stress state due to expansion and contraction of atoms (not considering dislocations and vacancies effects).

LIU et al [16] believed that the coherent or semi-coherent interface cannot form when the difference of the surface electron densities between the new phase atoms and the parent phase atoms is more than 10%. But this speculation has no a theoretical basis and has not been confirmed by the fact. The electron density condition of the coherent or semi-coherent interface requires further investigation.

4 Results and discussion

Using the measured deflection values of the film and substrate bi-layer cantilever beams, the average internal stress in the films can be obtained using Eq. (1). Consequently, the distributed internal stresses in the films can be obtained using Eq. (2). The results of the film/substrate systems with different materials are shown in Fig. 3. In Fig. 3(a), the average internal stress in 0.5 μm-thick Cu films is abnormally small. This is likely

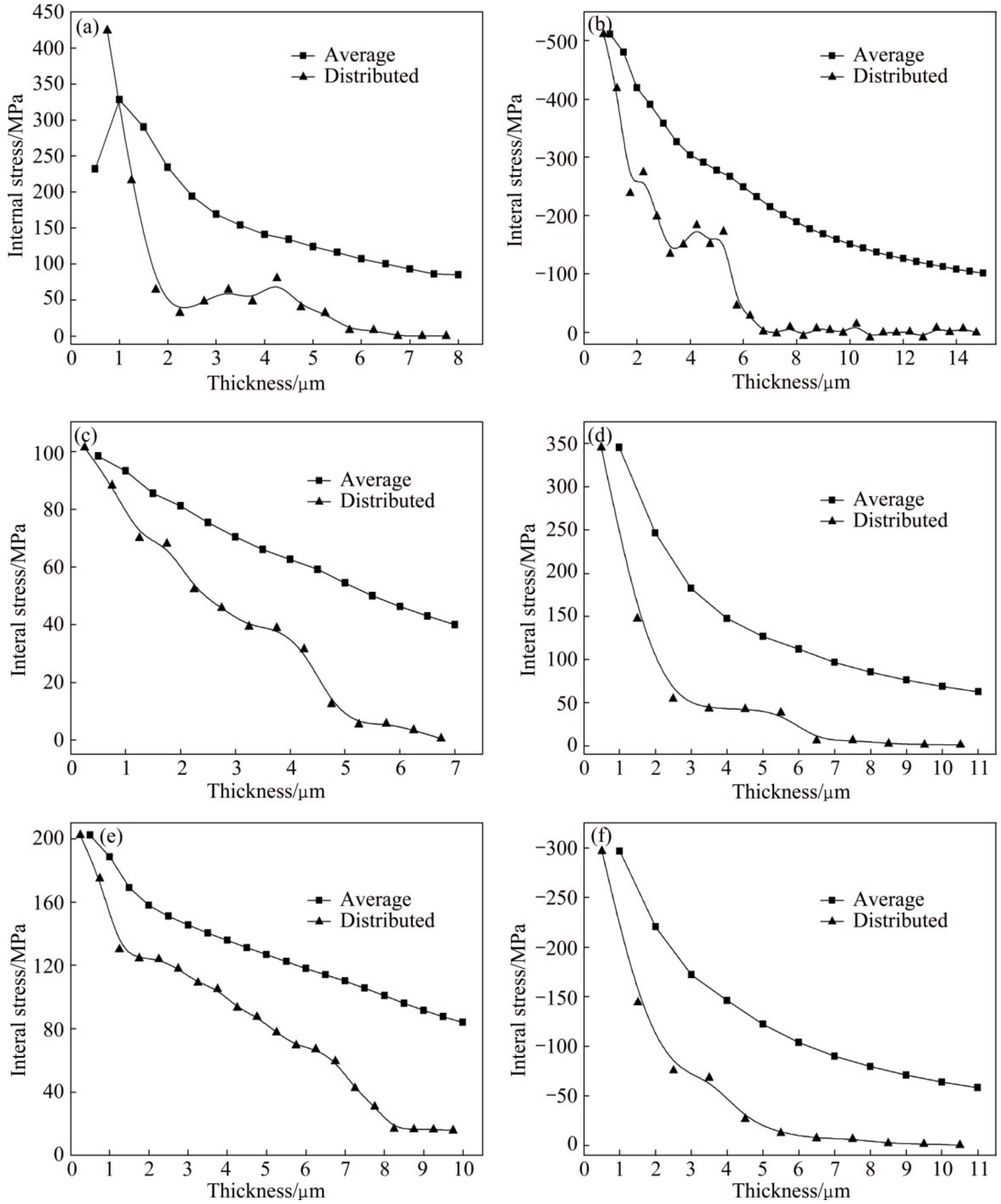

Fig. 3 Average and distributed internal stresses in films: (a) Cu films on Fe substrate; (b) Cu films on Ni substrate; (c) Cu films on Ag substrate; (d) Ni films on Fe substrate; (e) Ni films on Ag substrate; (f) Ag film on Cu substrate

to be caused by a larger measuring error of the smaller deflection of the cantilever beam with a smaller film thickness.

For the film/substrate systems with the same material, obvious bending deflection in the film and substrate bi-layer cantilever beams does not occur during electroplating (deflection values are zero, and then both of average and distributed internal stresses in the films are zero). Although the average and the distributed internal stresses in Cr films could not be obtained in experiment, it was seen that the Cr film on the Fe substrate bi-layer cantilever beam bends towards Fe substrate side. Thus, the average internal stress in Cr films is compressive.

As seen in Fig. 3, the average and distributed internal stresses in Cu films on Fe and Ag substrates, and in Ni films on Fe and Ag substrates are tensile, while those in Cu film on Ni substrate and in Ag film on Cu substrate are compressive. The substrate material has a great influence on the internal stress in the same films. Similar tendencies of the average and distributed internal stresses in Cu, Ni and Ag films are observed in Fig. 3, that is, these stresses decrease with the increase of the film thickness. The distributed internal stress of the films approaches 0 MPa when the films become thicker.

Since electroplating temperature is close to room temperature, there should be no or minimal thermal stress in all films; consequently, the internal stress in the films is the intrinsic stress. The distributed internal stress decreases with the increase of the film thickness, close to 0 MPa at the end. This shows that growth stresses in all the films with different material substrates are rather small and their internal stresses are mainly interfacial stresses. Thus, the bending deflection of all the film and substrate bi-layer cantilever beams is subjected to the interfacial stress characteristic, which is the same as the average internal stress in the film. The interfacial stresses in Cu films on Fe and Ag substrates, and in Ni films on Fe and Ag substrates are tensile, while those in Cu film on Ni substrate and in Ag film on Cu substrate are compressive. The situation of Cr films is supposed to be similar to other films, and the interfacial stress in Cr films on Fe substrate is compressive. For the film/substrate system with the same material (Ag film on Ag substrate, Ni film on Ni substrate and Cu film on Cu substrate), obviously, the interfacial stress in the films is zero. It is well known that more additives in the electroplating solution result in a larger growth stress. In our experiments the smaller growth stress is due to having less or no additives.

In the Jellium (Wingner–Seitz) model, the electron densities on the atomic surface of Fe, Cu, Ni, Ag and Cr metal materials are 2.739×10^{29} m^{-3}, 2.931×10^{29} m^{-3}, 3.261×10^{29} m^{-3}, 2.027×10^{29} m^{-3}, and 2.572×10^{29} m^{-3}, respectively [17]. According to the TFDC electron theory, and comparing the electron densities between the film and the substrate, in Cu film/Fe substrate, Cu film/Ag substrate, Ni film/Fe substrate and Ni film/Ag substrate systems, the interfacial stresses in the films are tensile and in substrate are compressive; in Cu film/Ni substrate, Ag film/Cu substrate and Cr film/Fe substrate systems, the interfacial stresses in the films are compressive; in Ag film/Ag substrate, Ni film/Ni substrate and Cu film/Cu substrate, the interfacial stresses in the films are zero. The result is the same from the experiments. This shows that the TFDC electron theory can expound the physical essence of interfacial stress and is applicable in the interfacial stress studies.

The new information in this work is in the form of uniting theory and experiment, and, to the best of our knowledge, no papers existing do this. Voids (dislocations and vacancies) within the film are considered as contributors to stress, according to the electron theory. However, dislocations and vacancies are part of the microstructure, which also contributes to stress. Proper microstructure characterization at this scale is challenging, and will be subject of a future study.

5 Conclusions

1) In electroplated Cu, Ni, Ag and Cr films with different materials with substrates, the growth stresses are very small and the interfacial stresses are the main stresses. In electroplated Ag, Ni and Cu films with the same material with substrates, the interfacial stresses are zero.

2) The interfacial stress characteristics of all electroplated films obtained from experimental results are consistent with those predicted based on the modified Thomas−Fermi−Dirac electron theory.

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基于电子理论的电镀薄膜内应力分析

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摘 要：用电镀方法在 Fe、Ni 和 Ag 基体上沉积 Cu 膜，在 Fe 和 Ag 基体上沉积 Ni 膜，在 Cu 基体上沉积 Ag 膜，在 Fe 基体沉积 Cr 膜，以及在 Ag 基体上沉积 Ag 膜，在 Ni 基体上沉积 Ni 膜和在 Cu 基体上沉积 Cu 膜。采用悬臂梁法原位测量了除 Cr 膜外其他薄膜的平均内应力。结果表明，薄膜和基体为异种材料时薄膜内界面应力很大，而为同种材料时界面应力为零。由悬臂梁的弯曲方向得到的界面应力的性质与由改进的 Thomas−Fermi−Dirac 电子理论得到的结果一致。

关键词：金属薄膜；沉积；界面；内应力；电子密度

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