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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: $CuSO_4\cdot 5H_2O$ (200 g/L), H_2SO_4 (60 mL/L) and HCl (1 mL/L); for Ag film: $AgNO_3$ (44 g/L), $Na_2S_2O_3\cdot 5H_2O$ (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: $NiSO_4\cdot 7H_2O$ (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·cm^{-2})	Deposition rate/(nm·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

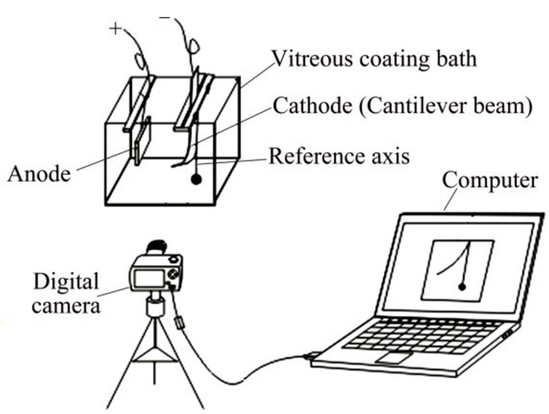

Fig. 1 Schematic illustration of in-situ internal stress measurement in films [13]