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STRESS-RELATED EFFECTS IN THIN FILMS

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Note: This summary article first appeared in the Proceedings of the 22nd Annual Technical Conference of the Society of Vacuum Coaters in 1979. It is reproduced here, with permission, for both its technical and historical significance. In it are found a number of the insights and instructive sketches characteristic of John Thornton, which in this case were known only to those few having access to the proceedings volume.

Virtually all vacuum-deposited coatings are in a state of stress. The total stress is composed of a thermal stress and an intrinsic stress. The thermal stress is due to the difference in the thermal expansion coefficients of the coating and the substrate materials. The intrinsic stress is due to the accumulating effect of the crystallographic flaws that are built into the coating during deposition. In soft, low melting point materials such as aluminum, bulk diffusion tends to relax the internal stresses and to prevent their accumulation. However, these diffusion processes can cause flaws such as holes and hillocks to form. In hard, higher melting point materials such as chromium deposited at low temperatures (*e.g.* the case of decorative coatings on plastic substrates), intrinsic stresses accumulate and tend to dominate over thermal stresses. Stress cracking and buckling are commonly observed. The fundamental nature of the internal stresses that are found in both evaporated and sputtered coatings is reviewed in this paper from the point of view of decorative coating applications. Recent sputtering studies are described which indicate that apparatus geometry is particularly important in determining the state of stress that forms in deposits.

1. INTRODUCTION

Virtually all metallic and inorganic compound films are in a state of stress. This behavior is independent of the method of deposition and applies, for example, to evaporated films[1]. The total stress is composed of a thermal stress and a so-called intrinsic stress. The thermal stress is due to the difference in the thermal expansion coefficients of the coating and substrate materials. The intrinsic stress is due to the accumulating effect of the crystallographic flaws that are built into the coating during deposition.

The internal stresses in a thin film can give rise to seemingly unrelated behavior that can seriously influence the film's performance. The parameter T/T_m, where T (K) is the substrate temperature and T_m is the coating material melting point, is particularly important in cataloging stress-related behavior for differing materials. In soft, low melting point materials such as aluminum, typical deposition conditions involve a relatively high T/T_m. Under these conditions, bulk diffusion, which becomes increasingly important with increasing T/T_m, relaxes the intrinsic stresses and prevents their accumulation. However, the thermal stresses resulting from the temperature changes which occur at the conclusion of deposition or in subsequent annealing cycles can drive these diffusion processes in such a way that material transport occurs, and holes and hillocks are produced in the films. In hard, higher melting point materials such as chromium, typical deposition conditions involve a relatively low T/T_m. Under these conditions intrinsic stresses can accumulate and dominate over thermal stresses.

The film-to-substrate bond must be capable of withstanding the force produced by the integrated stress throughout the film. In the intrinsic stress case this force increases with the film thickness and can be much larger than the forces provided, for example, by a typical tape adhesion test. Thus stress cracking, buckling, and poor adhesion are commonly observed when the film thickness exceeds a critical value which may be as low as several hundred ångströms.

The purpose of this paper is to review some of the considerations that are important in the occurrence of stresses in metal coatings. The discussion is generally from the point of view of decorative coatings. Thus particular emphasis is given to the stress-related effects that occur when brittle, high temperature coatings such as chromium are deposited on low temperature substrates such as acrylonitrile butadiene styrene (ABS). Recent sputtering studies will be described which indicate that the apparatus geometry is particularly important in determining the state of stress that forms in such coatings.

2. GENERAL ASPECTS OF THERMAL AND INTRINSIC STRESSES

2.1. Thermal stresses

When a coated substrate is at a temperature that is different from its temperature during deposition, a thermal stress will be present as a result of the differences in the film and substrate thermal expansion coefficients. For the thin films used in decorative coatings, the film thicknesses are generally less than 10^{-4} times the substrate thickness. Under these conditions, plastic flow in the substrate can generally be neglected and the thermal stress induced in the film by the film substrate bonding is given in a one-dimensional approximation (neglecting the Poisson effect) by[2,3]

$$\sigma_{th} = E_f(\alpha_f - \alpha_s)(T_s - T_a) \tag{1}$$

where E_f is Young's modulus, α_f and α_s are the average coefficients of thermal expansion for the film and substrate, T_s is the substrate temperature during deposition, and T_a is the temperature during measurement. A positive value of σ_{th} corresponds to a tensile stress.

Table I gives elastic constants and thermal expansion coefficients for several coating metals. Table II gives thermal expansion coefficients for typical substrate materials encountered in decorative coating. There seems to be no evidence that the thermal expansion coefficient[2] and the modulus of elasticity[3] for a film are very different from the bulk values. Thus the values given in the table may be used for making engineering estimates.

TABLE I
PROPERTIES OF COATING MATERIALS

Material	Melting temperature (°C)	T/T_m [a]	Young's modulus E_f (GN m^{-2})	Yield strength (GN m^{-2})	Thermal expansion coefficient (°C^{-1})
Al	660	0.34	63	0.11	2.39×10^{-5}
Sb	630	0.35	80	0.011	0.9×10^{-5}
Cr	1875	0.15	260	0.16	0.62×10^{-5}
Cu	1083	0.23	120	0.32	1.65×10^{-5}
Au	1063	0.23	81	0.21	1.62×10^{-5}
Fe	1534	0.17	204	0.25	1.17×10^{-5}
Pb	325	0.53	16	0.009	2.93×10^{-5}
Ni	1453	0.18	208	0.32	1.33×10^{-5}
W	3410	0.08	351	1.8	0.43×10^{-5}

[a] Based on $T = 40\,°C$ (typical deposition temperature on plastic substrate).

TABLE II
PROPERTIES OF SUBSTRATE MATERIALS

Material	Heat distortion temperature (°C)	Thermal expansion coefficient (°C^{-1})
ABS	95	9.5×10^{-5}
Polypropylene	85	8.5×10^{-5}
Nylon (mineral filled)	175	7×10^{-5}
Polyester (glass filled)	250	3×10^{-5}
Glass (soda–lime)	700 [a]	0.92×10^{-5}

[a] Softening point.

Consider the case of a thin chromium film ($\alpha_f = 0.62 \times 10^{-5}\,°C^{-1}$) deposited on an ABS substrate ($\alpha_s = 9.5 \times 10^{-5}\,°C^{-1}$) at a temperature of 40 °C (104 °F) and heated to 82 °C (180 °F) during a typical thermal cycle test for chromium-coated plastic automotive parts. A tensile stress of about 0.97 GN m^{-2} (140 000 lbs in^{-2}), which is larger than the yield strength of the chromium (0.16 GN m^{-2}) is predicted.

Next consider the case of an aluminum coating ($\alpha_f = 2.4 \times 10^5\,°C^{-1}$) deposited on a silicon substrate ($\alpha_s = 7.6 \times 10^{-6}\,°C^{-1}$) at a temperature of 150 °C (302 °F) and then annealed at 400 °C (752 °F) as part of an electronic processing application. A compressive stress of about 0.26 GN m^{-2} (37 000 lbs in^{-2}), which is larger than the yield strength of aluminum (0.11 GN m^{-2}), is predicted.

Thus we see that in many applications temperature differences between the

conditions of deposition and application, or associated with post-deposition annealing processes, can result in thermal stresses that exceed the yield strength of the film and are capable of fracturing even relatively strong coating-to-substrate bonds.

2.2. Intrinsic stresses

The intrinsic stress can be defined as that component of the total measured stress that cannot be attributed to thermal stress[4]. It is due to the accumulating effect of the crystallographic flaws that are built into the coating during deposition. The intrinsic stresses are similar to the internal stresses that are formed in a bulk material during cold working. In the cold work case, the stresses result from the strain which is associated with the various lattice defects created by the deformation. However, the density of defects that are frozen into a film during deposition can be two orders of magnitude higher than that produced by the severest cold-work treatment of a bulk material[3]. Intrinsic stresses that are in the range $0.1-3 \text{ GN m}^{-2}$ (15 000–450 000 lbf in^{-2}), and therefore comparable with the yield strength of most metals, can develop in thin films deposited at low T/T_m. The intrinsic stresses are strongly dependent on the conditions of deposition.

2.3. Recovery and recrystallization

The energy which is stored in a film or cold-worked metal by the stresses acts as a thermodynamic driving force which tends to relax the stresses (by vacancy, interstitial, and dislocation movement) if the temperature is such that T/T_m is in the range 0.1–0.3. The phenomenon is known as recovery[5,6]. At higher T/T_m (0.3–0.5), the stresses are relaxed by the recrystallization of the strained grains into new strain-free grains[5,6]. Thus at substrate temperatures such that T/T_m is greater than 0.2, recovery and recrystallization relax the intrinsic stresses and reduce their accumulation in a growing coating.

2.4. Influence of deposition conditions

The microstructure and thus the intrinsic stresses in vacuum-deposited coatings are sensitive to the deposition conditions. Figure 1 shows a schematic representation of the microstructure dependence of sputtered coatings on T/T_m and on the pressure of the argon working gas[7]. The growth of vacuum-deposited coatings involves atoms (1) arriving in a distribution that depends through self-shadowing on the coating atom arrival directions, and on the roughness of the coating surface, and then (2) diffusing over the surface until they become trapped in low energy lattice sites and are incorporated into the growing coating. Finally, the deposited atoms may readjust their positions within the coating lattice by recovery and recrystallization.

The T/T_m dependence in Fig. 1 results because the surface diffusion processes, like the bulk diffusion processes that characterize recovery and recrystallization (see Fig. 3(c)), are dependent on T/T_m. The pressure dependence is believed to result because collisions between the sputtered atoms and the argon atoms at elevated pressures cause the coating atoms to arrive at the substrate in randomized directions that promote shadowing.
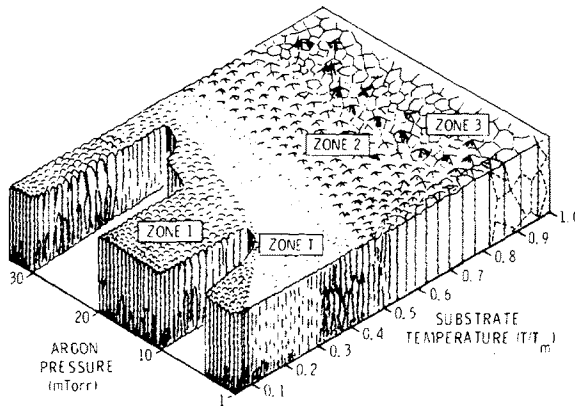
Fig. 1. Schematic representation of the influence of substrate temperature and argon pressure on the microstructure of metal coatings deposited using cylindrical magnetron sputtering sources. T (K) is the substrate temperature and T_m (K) is the melting point of the coating material. (See ref. 7.)

Coatings in the zone T (transition) region have a dense fibrous structure with a smooth, highly reflective surface. They form on smooth substrates at low T/T_m when the coating flux arrives in a direction that is largely normal to the substrate surface, so that shadowing effects are minimized. Coatings with the zone T structure are desired for decorative applications. Large intrinsic stresses can form in the zone T region.

Coatings in the zone 1 region are characterized by a structure consisting of tapered crystals separated by open, voided boundaries. The structure results from shadowing because high points on the growing surface receive more coating flux than valleys do, particularly when a significant oblique component is present in the arriving coating flux. This structure is promoted by an elevated working gas pressure or a substrate surface that is rough or is arranged at a large angle relative to the coating flux. The extreme zone 1 structure is too porous to support stresses and has a rough, poorly reflecting surface.

The zone 2 structure consists of columnar grains separated by distinct, intercrystalline boundaries. Recovery limits the intrinsic stresses in zone 2.

Zone 3 is defined as that range of conditions where bulk diffusion has a dominant influence on the final structure of the coating. Recrystallization occurs if sufficient strain is built into the coating during deposition. Recovery and/or recrystallization limits the intrinsic stresses in this region.

2.5. T/T_m influence on internal stress

Figure 2 shows an idealized representation of the total stress generated in a thin film as a function of T/T_m (ref. 2). The substrate temperature T is assumed to be greater than the final measurement temperature (room temperature), and the film thermal expansion coefficient is assumed to be greater than that of the substrate, so that a tensile thermal stress is generated (see eqn. (1)) when the substrate is cooled. The intrinsic stress is also assumed to be tensile (generally the case in evaporated films). At low T/T_m, the intrinsic stress dominates over the thermal stress. When

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