Microstructural Origins of Saccharine Induced Stress Reduction in Electrodeposited Ni

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Motivation—The majority of high-strength electrodeposited Ni films form with large tensile intrinsic stress. To reduce the tensile stress, and increase the engineering yield strength, mM/l concentrations of sulfur containing additives are included in the electroplating baths. However, prior to this work there had been no direct observations as to the fundamental mechanism through which saccharin, a common industrial stress reducing additive, and in turn sulfur, reduce the deposition stress in electrodeposited Ni.

Accomplishment—Previously we developed a technique to decouple the geometrically limited tensile island coalescence stress from the kinetically limited compressive stress generation mechanism. This technique is based on the combination of *in situ* stress measurement and through-mask electrodeposition of Ni thin films, as shown in Figure 1. By electrodeposition through a photoresist mask a periodic array of identical island was created. The resultant control over the geometry allowed the correlation of the thin film growth stages with the stress evolution.

The solid curve in Figure 2 is a typical stress evolution profile taken using this technique. As seen in the figure, during the initial stages of growth the stress was nominally zero, indicative of island growth through and over the photoresist layer prior to contacting the neighboring island. At the moment the neighboring islands contact, the systems undergoes a rapid tensile rise, which we previously demonstrated to be the result of elastic deformation of the islands towards each other. This behavior is similar to that observed during coalescence of soap bubbles, where, to minimize the total surface energy, a lower energy boundary is formed at the expense of an increase in total surface area. In the case of metal islands where shear stresses can be supported, the deformation of the island during coalescence induces a tensile stress, the magnitude of which is proportional to the difference in surface and grain boundary energy.

In the new work presented here, we used this technique to study the impact of saccharin on the island coalescence process. The dashed line in Figure 2 shows the dramatic shift in the stress evolution when saccharin was added to a Ni plating solution. As seen in the figure, the "saccharin" film immediately became compressive (negative) starting at the moment of coalescence, indicating that saccharine directly impacted the generation of stress during coalescence. In further experiments, we demonstrated that the kinetically limited compressive stress mechanism was unaffected by saccharin and that the magnitude of the compressive stress was directly dependant on the saccharin concentration in the bath. Therefore, we concluded that saccharin reduced the driving force for island coalescence by decreasing the difference in the grain boundary free surface energies. This is not to say that the coalescence stress was eliminated, rather the compressive stress mechanism became dominant when the tensile island coalescence stress was reduced by saccharin.

Significance—For nearly a half century saccharin has been added to Ni plating baths to reduce stress, but the mechanism through which this stress reduction occurred was unknown. This work provided the first direct evidence as to the fundamental mechanism active in this process and identified a previously unobserved intrinsic stress reduction mechanism.

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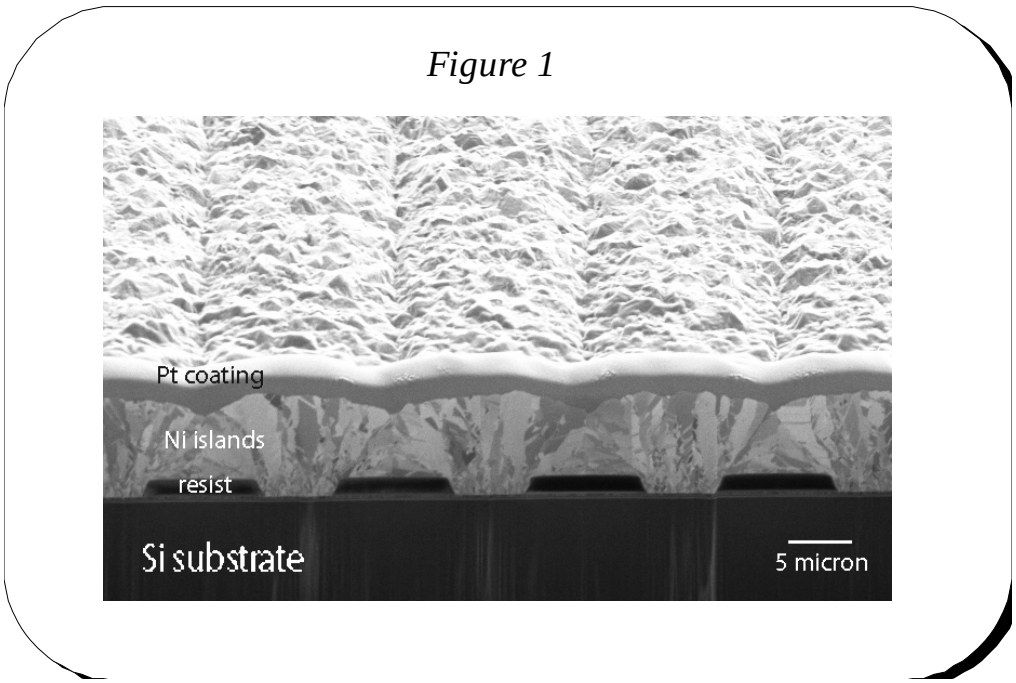

Figure 1. Obliquely viewed focused ion beam (FIB) cross-sectional image of a series of islands well after initial coalescence.

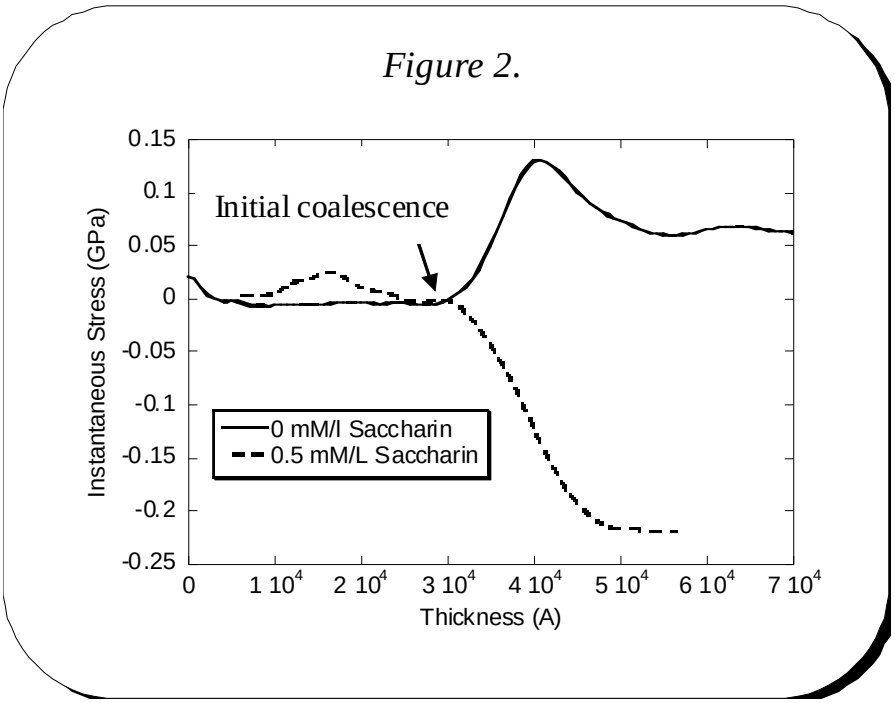

Figure 2. Stress as a function of film thickness taken during electrodeposition of the film. The arrow indicates the initial moment the islands contact in both plots. The solid curve is the Ni plated without additives and shows a strong tensile (positive) rise associated with the coalescence, whereas the dashed curve, Ni plated with saccharin, goes directly into compression with no tensile stress created during island coalescence.