

Analysis of stress/strain in Electroless Copper Films

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Abstract

Polymer substrates were chemically coated with copper using various electroless copper baths and the internal strain/stress, as well as the adhesion quality, in the resulting copper films were studied during and after deposition as a function of the deposit thickness and the operation parameters of the electroless bath. The appearance of internal compressive stress in the copper film correlates to the probability of buckle driven delamination failure (blistering). Based on a simple theoretical concept we derived limits of allowed compressive stress in the copper film without inducing this failure mode. Furthermore depth-resolved X-ray diffraction (XRD) measurements in up to 1 μm thick electroless films indicate an approximately linear internal stress profile from about +200 MPa tensile stress at the substrate/adsorbate interface to -100 MPa compressive stress at the surface of the deposit. This will be explained in terms of a possible composition gradient of nickel in the copper film.

Introduction

Electroless copper plating is a key process to provide seed layers on insulated organic substrates for the subsequent copper electroplating in printed circuit boards (PCB). The demand for even higher circuitry densities, lower power dissipation at higher temperatures and high signal frequencies on PCBs necessitate the application of smoother substrates. Various kinds of new organic substrate materials that have been introduced, are prone to spontaneous delamination failure modes (blistering) of the electroless layer during deposition. This failure is driven by the adhesion of the metal layer on the resin substrate, in terms of mechanical anchoring and chemical interface bonding, as well as thermal and intrinsic layer stress. For instance, the cool down process from electroless bath temperature to rinse water temperature is able to induce a substantial compressive stress [1], driven by coefficient of thermal expansion (CTE) differences of the

substrate and adsorbate, whereas storage at room temperature usually leads to an increase of tensile stress by self-annealing-induced densification of the films [2,3]. The dependency of stress evolution and blister generation enforces the general interest of the origin and adaptability of internal stress in electroless copper films and the interplay with adhesion parameters. From theoretical concepts internal *compressive* stress has to be a prerequisite for buckling-driven delamination (blistering) [4]. To prove the validity of stress-induced blistering, we perform experiments to correlate internal film stress and the probability of blister generation. The internal stress in the copper films, measured by XRD, is modulated in a wide range, by a variety of chemical bath compositions and bath temperatures. The second part of this paper presents observable dependencies of internal stress from film thickness and nickel content in the electroless bath, during and after deposition. We introduce a critical stress (σ_{crit}), as a limit for acceptable compressive stress without blister failure mode. In combination with

measured dependencies of internal stress most experimental observations of blister failure, e.g. the dependency of the failure mode on electroless film thickness, is explainable. A well-known impact parameter on internal stress, during copper deposition is the nickel content in the electroless bath. Nickel allows the adjustment of internal tensile film stress (pre tensile stress) so that the system can be kept from thermally-induced critical compressive stresses [1]. To investigate the origin of this impact of nickel on film stress we carried out depth-resolved stress profile analysis via XRD, combined with ICP-OES on these films.

Correlation of internal film stress with delamination failure mode (blistering)

The established theoretical model for the evolution of the blister failure mode is sketched in Fig. 1 [4]: if an initially weak or debonded microscopic interface region exists, in the interior of the film/substrate interface, that region will buckle away from the substrate if the residual compressive film stress is large enough. If the film buckles up from the substrate, the compression in the film near the edges is partially relieved and a moment of force M , with direction away from the surface develops. If M exceeds the existing clamp forces along the blister edges (defined as edge compression T in units force/length), the buckled area extends laterally. In this manner, the copper film formally “peels” from the substrate surface. It is obvious that the edge compression T can be assigned to the peel strength (PS in units force/length) of the copper film, a well-known measurand in the PCB industry. On the other hand PS depends on roughness, mechanical anchoring and chemical bonding to the substrate surface. A derivation from the fully nonlinear Karman plate equations, described in detail in [4], leads to a simple estimation of the critical compressive stress

$$\sigma_{crit} \approx PS/d_{Cu} \quad (1)$$

, where d_{Cu} is the thickness of the copper film. If the internal film stress is lower (that is, “more negative”) than σ_{crit} blistering delamination starts. Nevertheless, following this argumentation a prerequisite for the generation of blisters is compressive stress. To prove the validity of this model, we visually investigated the plated samples (substrate: acrylonitrile butadiene styrene (ABS), measured 12 h after deposition), classified them as “blistered” or “not blistered”, and obtained the internal stress in the copper films of these samples by XRD measurements. In terms of a screening experiment a wide spread of electroless bath compositions were tested, including copper, nickel, ammonia and formaldehyde concentration and two kinds of stabilizer systems. As a consequence of these changes, growth-inherent parameters, such as

growth rate and final film thickness were influenced, too. The result of this experiment is shown in Fig. 2. An unambiguous assignment of “blistered” and “not blistered” groups to the kind of stress is observable: all samples with compressive stress show blisters, whereas all samples with tensile stress have no indications of this failure mode. This result can easily be interpreted in terms of the blister evolution model: the tensile stress is ranging from +10 MPa to +80 MPa and from the blister model it is expected that generally tensile stress excludes the generation of blisters - this prediction is confirmed.

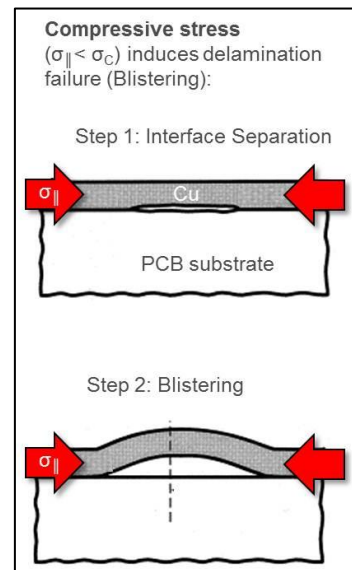


Figure 1. Theoretical explanation of blister evolution: if the internal film stress ($\sigma_{||}$) is lower, by meaning of “more negative”, than a critical compressive stress (σ_{crit}), the copper film delaminates from the substrate (primarily on local regions with low adhesion) and buckles.

In the range of compressive stress it depends on σ_{crit} if delamination occurs or not. The measured substantial compressive stress, from -30 MPa to -140 MPa, apparently higher than the critical limit, results at the end in the formation of blisters. Finally it is experimentally confirmed that a driving force for the evolution of blisters is compressive internal film stress.

Dependencies of the internal film stress from copper film thickness and nickel content in the electroless bath

It is well known, that in the case of electroless deposition the probability of delamination failures rises with increasing film thickness. Fig. 3 presents a summary of measured internal film stresses (12 h after deposition) over deposited copper film thickness, for various electroless baths (each bath is marked by color). The spread of stress values for

the same film thickness is substantial, due to different growth-induced film stresses, by different electroless bath types. Nevertheless a broad monotonic decrease of tensile stress by increased film thickness is observable. In the thickness range up to $0.5\ \mu\text{m}$ the final internal stress state for electroless copper films lies in an interval of $+(0.2\pm 0.1)\ \text{GPa}$ (tensile stress), whereas at about $2.5\ \mu\text{m}$ the stress values range is $(0\pm 0.05)\ \text{GPa}$. The final stress state depends on the internal stress implemented during growth, thermal stress after cooling from deposition temperature and recrystallization effects during storage time, and can thus significantly deviate from the initial internal stress during growth. Exemplarily, the red shaded curve in Fig.3 marks the critical compressive stress σ_{crit} for a PCB-typical PS of $5.0\ \text{N/cm}$. Internal film stresses lower than σ_{crit} achieve the condition for blistering. Hence, for layer thicknesses higher than about $2\ \mu\text{m}$, most of the deposits of the tested electroless baths, would fulfill this condition of delamination failure. In this context the usually observed higher probability of generating blisters with increasing thickness seems reasonable.

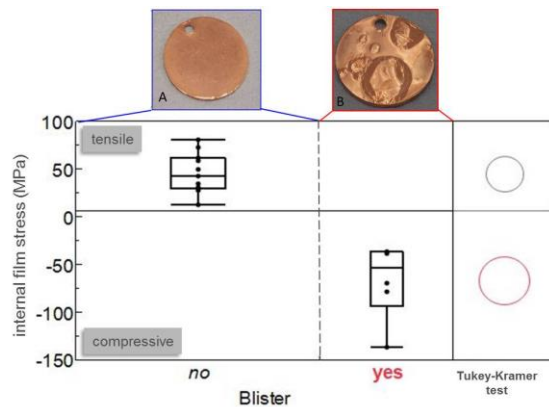


Figure 2. Correlation of internal film stress and the generation of blisters: all samples with compressive stress are blistered, whereas the full set of blister-free samples show tensile internal stress, this confirmed the blister model in Fig.1

Moreover from Fig.3 (intuitively known) strategies are extractable to avoid blistering: (1) implement during growth a high pre-tensile stress in the electroless film (e.g. by enhanced nickel content) (2) reduce film thickness and (3) increase deposit/substrate adhesion. The latter will shift the red curve $\sigma_{\text{crit}}(d_{\text{Cu}})$ downwards to higher compressive stress values. This will be highly effective especially in the thickness range lower than $1.0\ \mu\text{m}$. For instance the enhancement of PS from $3.0\ \text{N/cm}$ to $8.0\ \text{N/cm}$ in case of a $0.5\ \mu\text{m}$ thick electroless film, results in a shift of compressive critical stress of $\Delta\sigma_{\text{crit}} = -0.1\ \text{GPa}$,

whereas the same gain in PS at a film thickness of $1.5\ \mu\text{m}$ leads to a comparatively negligible shifting of $\Delta\sigma_{\text{crit}} = -0.02\ \text{GPa}$. A similar approach is valid for stress evolution during growth. The possibility of modifying the internal stress of electroless copper films during growth by chemical (nickel and cyanide concentration, stabilizers etc.) and thermal control of the electroless bath has been suggested based on the results of previous investigations [3,4]. Higher nickel concentration, for instance, results in a substantially higher tensile stress of the films, although the proportion of nickel incorporated in the deposit typically amounts to just 1% (Figure 6). The origin of these impacts of nickel in electroless copper films is still the subject of intense debate, but nevertheless the nickel content in the bath can be used to adjust the copper film stress during growth over a wide range of some $100\ \text{MPa}$ from compressive to tensile stresses. Figure 4 shows the stress evolution during growth measured by *in situ* XRD (experimental details see [5]) for four different electroless copper baths with increasing nickel concentration from Bath 1 to Bath 4. The nickel content in Baths 2 and 3 is identical, but a different stabilizer is used in each.

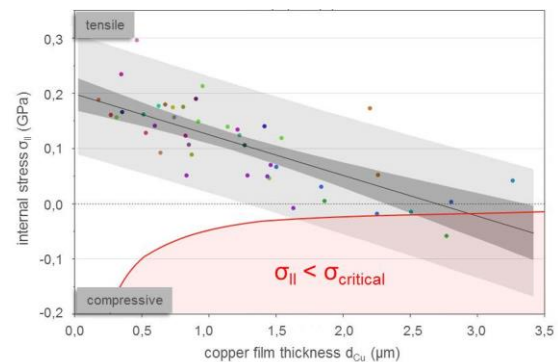


Figure 3. Dependency of internal film stress (12 h after deposition and measured by XRD at room temperature) from the thickness of the deposit: the coloration of the dots marks samples from different electroless baths and the red curve depicts the critical compressive stress $\sigma_{\text{crit}}(d_{\text{Cu}})$ for a typical PS value of $5.0\ \text{N/cm}$

For copper thicknesses beyond $0.3\ \mu\text{m}$, the internal stress values are significantly different from bath to bath with a high reproducibility. Furthermore, the following trends can be observed: films on rigid smooth ABS substrates with thickness larger than about $0.6\ \mu\text{m}$, and stress in the range from $+50$ to $-300\ \text{MPa}$, have a high probability for blister generation. In contrast, for films with tensile stress above $100\ \text{MPa}$ adhesion does not fail.

Typically blisters evolve after subsequent water rinsing and drying after deposition. As discussed before, blistering is common and a well-known adhesion failure mode indicative of the tendency of a deposit to compensate for compressive film stress. Such behavior in relaxed or slightly tensile-stressed electroless films (that is, outside of the critical compressive stress condition, red shaded area in Fig. 4 with $PS=5.0$ N/cm) at first appears surprising. The explanation for this effect lies in the different CTEs of copper and ABS and hence the shrinking of the ABS substrate during the cooling from typical electroless bath temperatures (32 °C-47 °C, depending on the electroless bath used) to rinse water temperature (16 °C-18 °C). This thermal substrate shrinking can induce substantial compressive stress in the thin electroless copper film after deposition [1].

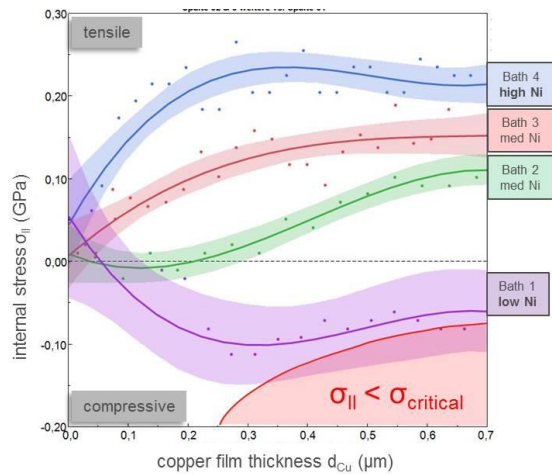


Figure 4. Plot of the internal stress of copper films deposited from the electroless copper baths 1-4 against deposit thickness, as measured by in situ XRD. The red curve depicts the critical compressive stress $\sigma_{crit}(d_{Cu})$ for a typical PS value of 5.0 N/cm

Nevertheless, the copper deposit from Bath 1 (with low nickel content) would directly fulfill the failure mode condition: $\sigma_{||} < \sigma_{crit}$, for thicknesses > 0.6 μm , during the growth, i.e. without additional thermal compressive stress afterwards. And indeed only the deposit in Bath 1 starts to evolve blisters at about 0.5 μm layer thickness *during growth*.

So we found a general trend of electroless copper films to reduce tensile stress with increasing film thickness and demonstrated the influence of nickel on internal stress during growth. The concept of a critical compressive stress, which depends on layer thickness and PS can be used to explain quantitatively the experimentally observed appearance of blister phenomena.

Depth-resolved stress profile of electroless copper films and the effect of incorporated nickel during growth

To understand the formation of internal stress in electroless copper films, we carried out depth-resolved XRD measurements. The variation of depth information in thin films is here achieved by a variable grazing X-ray incidence set up. The depth resolution of this method is restricted to some nm. This measurement is based on the analysis of the [11]-diffraction peak. For a detailed description of the measurement method and analysis we refer to [6,7]. The used sample geometry was 5 cm \times 5 cm square and 5 mm thick desmeared ABS samples coated with 0.5 μm and 1.0 μm thick electroless copper, deposited from Bath 3 (see Fig. 4) with a medium nickel content of 400 ppm. The results for both samples are shown in Fig. 5.

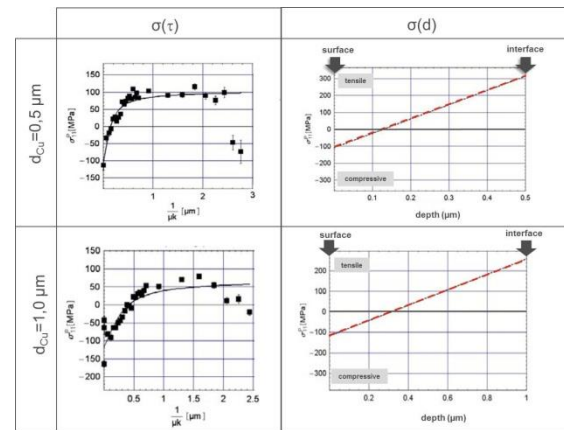


Figure 5. Depth-resolved stress profile of a 1.0 μm and 0.5 μm thick electroless copper film. Compressive stress at the surface and tensile stress at the interface of the film are evident.

The left side of Fig. 5 depicts the measured in-plane stresses in terms of $\sigma(\tau)$, where τ is the penetration depth of the $\text{CuK}\alpha$ -X-rays,

$$\tau = \frac{\sin^2 \theta - \sin^2 \psi + \cos^2 \theta \sin^2 \psi \sin^2 \eta}{2\mu \sin \theta \cos \psi} \quad (2)$$

θ is the Bragg angle, μ is the linear absorption coefficient of copper, η is the sample rotation angle around the scattering vector and ψ is the tilt angle to the surface normal vector. The successive fitting procedure to the experimental data works as follows: an assumed vertical stress profile of the biaxial internal stress in the real space ($\sigma(d)$, right side of Fig.5), described by a suitable mathematical function, e.g. polynomials, is transformed via Laplace transformation of equation (3) in the $\sigma(\tau)$ -form and compared to the experimental data.

$$\sigma_{ij}(\tau) = \frac{\int_0^D \sigma_{ij}(d) e^{-d/\tau} dd}{\int_0^D e^{-d/\tau} dd} \quad (3)$$

The total film thickness D can be set to infinity, due to extremely low penetration depth of the X-rays. The data show a similar vertical stress profile in both samples. In contrast to the substantial compressive stress of about -0.1 GPa in the region near to the surface, the middle depth range of the films indicates clear tensile stress of about +0.1 GPa in the 0.5 μm thick film (+0.05 GPa in the 1 μm thick sample). The assumed linear stress profiles for both samples reflect reasonably this tendency. Similar observations were made with the in-situ deposit stress analyzer (DSA) bending methods [8]. To explain the nearly linear increase of tensile stress from the surface of the electroless copper film to the substrate interface, we analyze the strain-free lattice parameter d_0^{111} of the (111)-lattice planes.

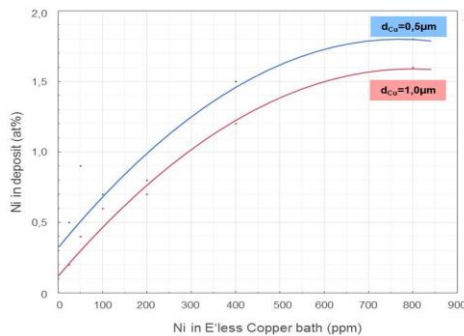


Figure 6. Plot of the percentage of nickel incorporated in the electroless copper deposit against the nickel content in the bath (in parts per million (ppm)) for two films of different thickness (0.5 and 1 μm).

Under the valid assumption of a simple biaxial stress state in the thin copper films, changes in d_0^{111} can directly be interpreted in terms of a chemical composition gradient in the electroless film. From this a continuous decreasing of the lattice parameter d_0^{111} from 0.2088 nm at the surface to 0.2084 nm at the substrate interface is measurable (by a measurement precision of ± 0.00002 nm), and gives a clear indication to a nearly linear chemical compositional gradient in the electroless film. From the comparison of the measured d_0^{111} parameter with bulk d^{111} values of copper (0.2088 nm) and of nickel (0.2034 nm), it seems reasonable that the incorporated fraction of nickel (about 1%, see Fig.6) in the electroless copper film leads to the observed compositional and finally to the vertical stress gradient. To prove the assumption of a film-thickness-dependent nickel incorporation during growth, we measured the incorporated nickel in a 0.5 μm and 1.0 μm thick electroless copper film as a function of nickel concentration in the electroless

bath, and found that the incorporated fraction in the thinner copper layer is always higher compared to the 1.0 μm thick layer. It seems that in the first stage of copper growth a significantly higher amount of nickel is incorporated in the electroless film, and causes higher tensile stresses in the region near the substrate interface. With increasing film thickness the nickel incorporation diminishes, thus resulting in lower tensile stresses in the upper regions of the copper film. A good way to confirm this nickel gradient is TOF-SIMS: measurements using this method are in progress.

Conclusion

The internal stress of electrolessly deposited copper films is a driving force of delamination failures, like blistering. Higher copper thickness generates more compressive stress and hence an increase of blister probability. On the other hand higher nickel contents in the electroless bath can prevent blistering during growth. Both features are quantitatively explainable by means of the critical compressive stress σ_{crit} . Furthermore we found a significant stress gradient from some -0.1 GPa (compressive) at the surface to +0.2 GPa (tensile) at the deposit/substrate interface in depth-resolved X-ray measurements. This nearly linear depth profile of internal stress in the electroless film is attributed to a gradient of incorporated nickel.

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