

Influence of pH value on microstructure and thermal stability of Ni–P electroless coating prepared in acidic condition

Xiao Wei Zhou^a, Hui Ming Jin^{a,*}, Lin Nan Zhang^b

^a College of Mechanical Engineering, Yangzhou University, Yangzhou 225009, China

^b College of Environmental Science and Engineering, Peking University, Beijing 100023, China

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Abstract

Three kinds of Ni–P electroless coatings were prepared in nickel sulphate solution at different pH values of 4.5, 5.5 and 6.5 with the purpose of ascertaining the influence of pH value on microstructure, internal stress statue and thermal stability of the coatings. Laser curvature (LC) method was used to measure the residual stress level in the coatings. Scanning electronic microscopy (SEM) and transmission electronic microscopy with energy dispersive spectrum (TEM/EDS) were used to examine the surface morphology and internal phase structure of the coatings, respectively. Differential scanning calorimeter (DSC) was used to analyze the phase transformation and thermal stability of the coatings at high temperature. Results showed the Ni–P coating prepared at pH 5.5 with nano-crystal mixed in amorphous structure had the worst thermal stability. The relatively higher stability of Ni–P coatings prepared at pH 4.5 and 6.5 was ascribed to the lower tensile stress level and much finer grain size, respectively. Besides, inverse Hall–Petch effect of annealing strengthening might also contribute to the integrity of Ni–P coating prepared at pH 6.5.

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Electroless deposited Ni–P coating has been widely used due to its excellent wear resistance, corrosion resistance and solderability [1,2]. In microelectronic package technology, the Ni–P coating is used as under bump metallurgy of solder in the manufacturing of flip chips, and its internal microstructure tends to transform during the solder hot flow process [3]. This transformation is usually accompanied by the depletion of Ni atoms, the precipitation of Ni₃P from the amorphous Ni–P phase and the new Ni₃Sn₄ phase at the solder/Ni–P interface. Although many research have been done on Ni–P coatings' preparation, corrosive property and tribological property [1–6], few has been reported on the relationship between its microstructure, P content, phase transformation at high temperature and internal stress status. In the present wok, the Ni–P coatings are prepared at different pH conditions and the above aspects are carefully investigated by several methods.

1. Experimental

Single crystal silicon [1 0 0] is used as substrate materials and is wire-cut to 0.5 mm × 10 mm × 40 mm specimens. After being finally grinded by 1200[#] SiC abrasive paper and polished by 0.2 μm Al₂O₃ abrasive paste, the

* Corresponding author.

E-mail address: doctorjhm@sohu.com (H.M. Jin).

Si specimens are vacuum-sputtered a Cu film of 1 μm thickness on one side (10 mm \times 40 mm face) for further Ni–P deposition. All specimens are ultrasonically cleaned in acetone and rinsed in 3 wt% HCl solution 10 s for activation immediately before the depositing process. The electroless Ni–P depositing bath is composed of 32 g/L nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), 25 g/L sodium hypophosphate ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$), 12 g/L sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), 5 mol/L phosphoric acid and 0.1 g/L sodium laurel sulphate. The depositing temperature is set at 85 $^\circ\text{C}$ and the pH value is controlled by adding H_2SO_4 or NaOH solutions to the electroless bath. Scanning electronic microscopy (SEM) is used to examine surface morphologies of coatings. Transmission electronic microscopy equipped with energy dispersive spectrum (TEM/EDS) and differential scanning calorimeter (DSC) are used to study the coating's phase structure as well as the phase transformation at high temperature.

2. Results and discussion

Three kinds of electroless Ni–P coatings are prepared at different pH values of 4.5, 5.5 and 6.5, respectively, and their SEM surface morphologies are shown in Fig. 1. During the experiment, it is found that lower pH condition can result in higher depositing speed. So the actual depositing time at pH values of 4.5, 5.5 and 6.5 are 60, 70 and 85 min, respectively, to ensure these Ni–P coatings of the same thickness of 15 μm for further residual stress evaluation by laser curvature (LC) method.

In Fig. 1 we can find obvious hump character on Ni–P prepared at pH 4.5, some nodules character on Ni–P prepared at pH 5.5 and flat character on Ni–P prepared at pH 6.5. It is commonly recognized the hump and nodules feature is related to the internal stress accumulation during the depositing process [2,4]. EDS testing shows the P contents in these three coatings are 12.5, 8.4 and 4.6 wt%, respectively.

Laser curvature method is used to evaluate the stress level in coatings by using Stoney's equation [1,3]:

$$\sigma_f = \frac{Y_s t_s^2}{6t_f} K \quad (1)$$

where σ_f is the average stress level in Ni–P coating, Y_s is Young's modulus of substrate Si plate, t_s and t_f are thickness of the substrate and the coating, respectively, and K is the curvature of the specimens. The calculated biaxial stress values in three Ni–P coatings prepared at pH 4.5, 5.5 and 6.5 condition are 126, 251 and 326 MPa, respectively, and all are tensile stress.

Fig. 2 is the TEM bright field images of three Ni–P coatings as-deposit. We can find the Ni–P coating prepared at pH 4.5 has pure amorphous structure, the Ni–P prepared at pH 5.5 has some nanometric crystal mixed in amorphous structure and the Ni–P prepared at pH 6.5 has entire nanometric structure; Meanwhile, the Ni crystal in the pH 6.5 condition in Fig. 2(c) is much finer than its counterpart in pH 5.5 condition in Fig. 2(b).

Differential scanning calorimeter is used to examine the phase transformation in Ni–P coatings at elevated temperature and the result is shown in Fig. 3. During the experiment the scanning rate is 20 $^\circ\text{C}/\text{min}$ and high purity Ar is used as protective gas. The DSC curves of the three Ni–P coatings all have two exothermic peaks.

In the pH 4.5 and 5.5 cases, the first peak corresponds to the Ni crystal precipitation from the amorphous phase, and the second peak corresponds to the Ni_3P phase precipitation from the former Ni crystal and the amorphous phase. We shall note the decrement of the first peak's intensity and width when pH value changes from 4.5 to 5.5, which illustrates

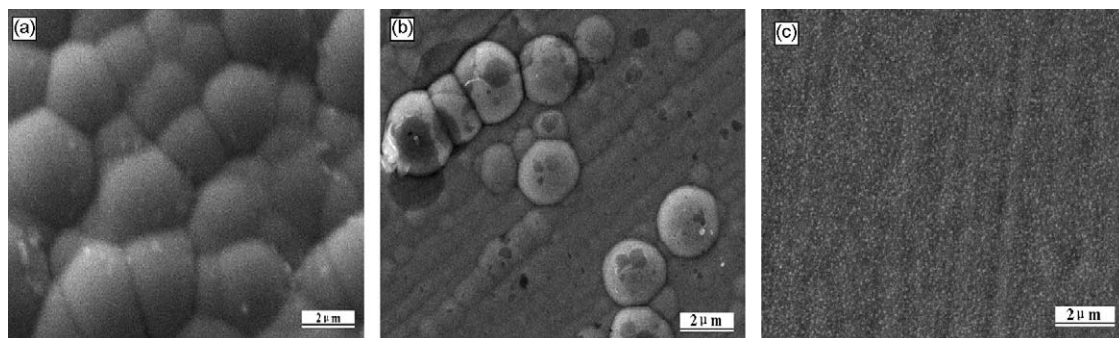


Fig. 1. SEM surface morphologies of Ni–P coatings prepared at pH values of 4.5 (a), 5.5 (b) and 6.5 (c).

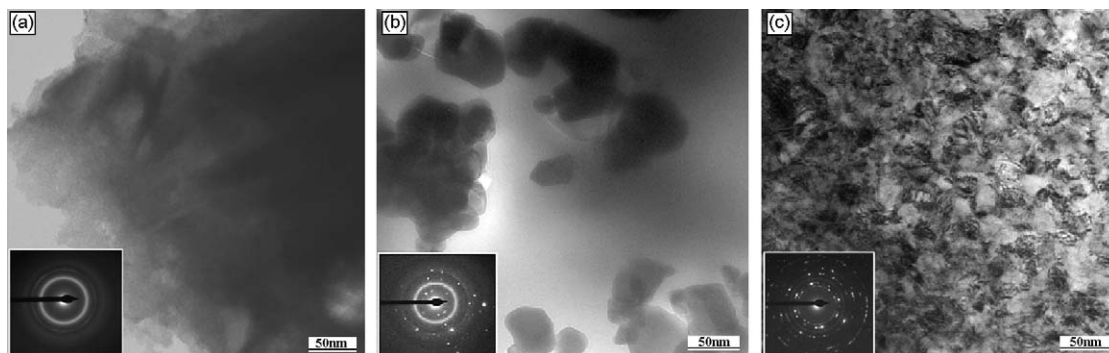


Fig. 2. TEM bright field image and electron diffraction pattern of Ni-P prepared at pH 4.5 (a), 5.5 (b) and 6.5 (c).

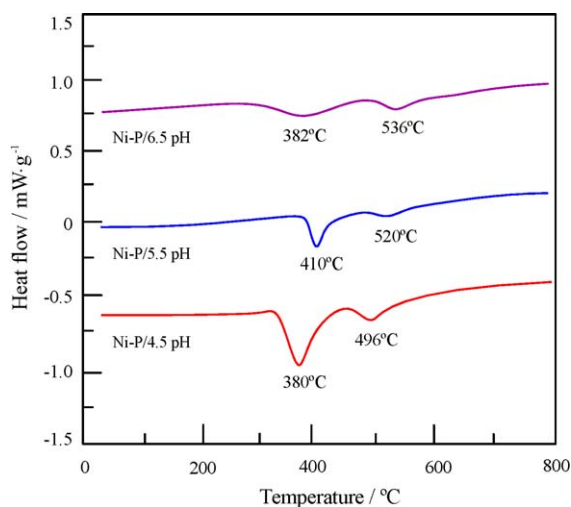


Fig. 3. DSC curves of Ni-P coatings prepared at different pH condition.

the intrinsic metastability of the amorphous structure and its tendency to decompose by solid-state diffusion at high temperature. As to the phase precipitation temperature, 327–440 °C has been reported for the Ni precipitation and 425–550 °C has been reported for the Ni₃P precipitation by different researchers [2–8], the large deviations are probably due to the more or less difference in their coating's preparation, such as in bath composition, temperature, substrate materials with different catalytic properties or additives, etc.

In the pH 6.5 case, the first peak corresponds to the nanometric Ni crystal's growing (conglomerating) and P segregation at Ni grain boundaries [4,6], and the second peak corresponds to the Ni₃P precipitation from Ni crystal. From the intensity and width of the first peak in pH 6.5 curve, we can find the nanometric Ni crystal's growing begins at much low temperature (about 300 °C) and proceeds at much wide temperature span.

After the DSC scanning up to 800 °C and furnace cooling to ambient temperature, some cracking has been found on Ni-P coating prepared at pH 5.5, while no obvious cracking has been found on Ni-P coatings prepared at pH 4.5 and 6.5. This phenomenon seems to disagree with the stress measurement by laser curvature method in which the highest internal tensile stress exists in the pH 6.5 as-deposit Ni-P coating.

In order to ascertain the originality of cracks in DSC-tested Ni-P coating prepared at pH 5.5, intentional thermal shock in Ar atmosphere (30 min heating at 250 °C + furnace cooling) is applied to the three as-deposit Ni-P coatings to evaluate their thermal stability in the absence of any possible influence from phase transformation. Thermal chock result seems to be the same, i.e. cracking on the Ni-P coating prepared at pH 5.5 and integrity on the Ni-P coatings prepared at pH 4.5 and 6.5. SEM and TEM are further used to examine the thermal-shocked Ni-P coating prepared at pH 5.5, and morphologies are shown in Fig. 4.

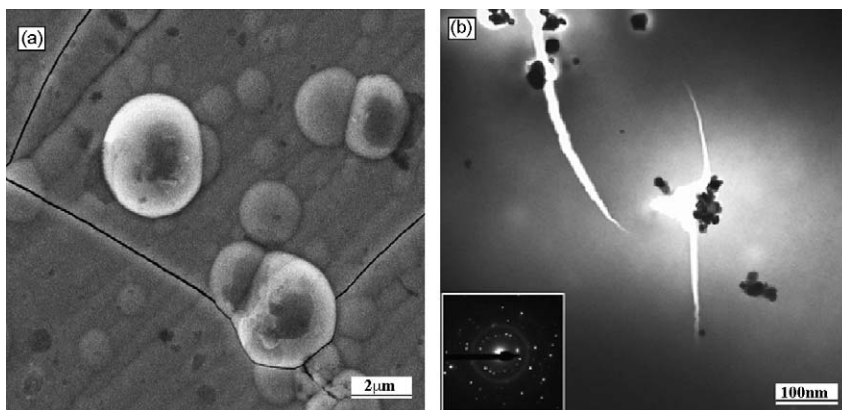


Fig. 4. SEM (a) and TEM (b) image of thermal-shocked Ni–P coating prepared at pH 5.5.

From Fig. 4(b) we can find the originality of tensile cracks in the coating. The crack seems to originate from the Ni/Ni–P interface and propagate within the amorphous Ni–P phase. Balaraju et al. [9] has reported the lower fracture toughness of the amorphous Ni–P phase compared with the P-oversaturated Ni phase, and this may contribute to the crack feature in our experiment. In addition, part of P previously solid-dissolved in metastable Ni–P amorphous phase may segregate to the Ni/Ni–P interface at high temperature and undermine the interfacial bonding.

The reason of the Ni–P coating prepared at pH 4.5 without cracking is due to its intrinsic low tensile stress and absence of Ni crystal or Ni₃P precipitation at 250 °C. Even Ni and Ni₃P precipitation happens at higher temperature as in the DSC experiment, the external-thermal-induced Ni crystal has much lower P content compared with the electroless as-deposited Ni crystal (EDS equipped in TEM results show the P concentration of 0.06 and 1.2 wt% in the two cases, respectively), the former Ni crystal has higher ductility than the latter and is more liable to relieve part of internal stress via deforming or creeping at high temperature, so this may be another reason for the integrity of the Ni–P coating prepared at pH 4.5 after the final 800 °C DSC scanning.

Although the Ni–P coating prepared at pH 6.5 has the highest stress level among the three as-deposit coatings, its homogeneous structure with much finer nanometric phase (Fig. 2(c)) can prevent any possible stress concentration. Besides, the electrolessly deposited phosphorus is homogeneously dissolved in nickel crystal phase without any Ni₃P precipitation, and this also attributes to the coating's high fracture toughness by the solid-dissolution strengthening mechanism. Another reason for its integrity after thermal shocking is probably due to the so-called “inverse Hall–Petch effect” reported by Huang [10], in which annealing strengthening phenomenon is recently been found in some bulk nanomaterials such as nano-Cu and nano-Ni, and this strengthening is come from the relaxation of grain boundaries, decrement of interior dislocation number and the accompanied increment of flow stress needed for the initial dislocation emitting.

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