Structural and Corrosion Properties of NiPₓ Metallic Glasses: Insights from EIS and DFT

Guofeng Cui,*† Jie Zhao,‡ Shaofang Liu,† and Gang Wu§

†Key Laboratory of Low-carbon Chemistry & Energy Conservation of Guangdong Province, School of Chemistry and Chemical Engineering, Sun-Yat Sen University, Guangzhou, 510275, People’s Republic of China
‡School of Mechanical and Automotive Engineering, South China University of Technology, Guangzhou 510640, People’s Republic of China
§Materials Physics & Applications Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States

ABSTRACT:

Despite the increasing interest in metallic glasses for a variety of engineering applications, the structure and corrosion properties still remain unknown. In particular, these properties for Ni–P alloy, a typical metallic glass, are greatly dependent upon the phosphorus content in the alloy. In this report, a relationship between the structural property and the interface corrosion behavior of Ni–P alloys was studied when phosphorus content was intentionally tuned. DFT calculation and EIS measurement were used to determine the electronic structure property and corrosion behavior of Ni–P alloy in acidic Au(III) solution that is applied to the immersion gold process of electroless deposited Ni–P alloys in the manufacture of printed circuit boards. The results indicate that the doped phosphorus atoms are able to bind electrons and change the structure of Ni–P alloy from the metallic to ceramic state, thereby avoiding an overetching in the solution. Theoretical calculation predicts that the anticorrosion ability of Ni–P alloy will be enhanced with phosphorus content. This is in good agreement with experimental data obtained in this work.

1. INTRODUCTION

Ni–P alloy, a kind of metallic glass, was discovered more than 40 years ago. Nowadays, Ni–P alloy has become an essential coating in the electroless nickel/immersion gold (ENIG) process for the printed circuit board (PCB) surface finish. Figure 1a shows the image of the PCB after ENIG treatment. During the process of ENIG, excessive corrosion of Ni–P alloy by gold ion can form a “black pad” between the alloy and gold layer, as shown in Figure 1b. It would result in a failure of PCB solderability. The black corrosion pits on the crystal grain, and black corrosion lines on the crystal boundary, are exposed after the gold layer stripped off, as shown in Figure 1c. Therefore, investigation on the corrosion behavior of Ni–P film in gold salt electrolyte is very important for the PCB industry. However, there is still no effective model to determine the correlation between the structural property and corrosion behavior of Ni–P alloy. Because of the disordered atomic arrangement, atomic structural models proposed previously were not successful to fully understand the effect of doped phosphorus atoms on the corrosion behavior of the alloys. Our recent works attempt to use a short-range ordered model of metallic glasses to study the electronic structural and corrosion behavior of a model Ni–P alloy. The combination of DFT and EIS methods has become an effective way to determine the correlation between the structural property and electrochemical reaction behavior. Thus, we illustrated the oxidation mechanism of hypophosphate anion in the formation process of amorphous Ni–P alloy by combining DFT and EIS methods. Although many papers have proposed that doped phosphorus content could affect corrosion characteristics of amorphous Ni–P alloys, the nature of such enhancement in corrosion resistance derived from doped phosphorus atoms remains unclear.
In this report, the effect of doped phosphorus atoms on the electronic structure property of Ni–P alloy was studied by the DFT method. In the meantime, corrosion behavior of Ni–P alloy in Au³⁺ solution was analyzed by the EIS method as a function of phosphorus content. On the basis of the theoretical and experimental results, an optimal phosphorus content for the ENIG process was proposed.

2. EXPERIMENTAL SECTION

2.1. Electrode Preparation. Copper sheets (20 × 50 mm² with a thickness of 0.5 mm) were used as substrates for electroless nickel deposition. The copper substrates were first degreased with 10% NaOH solution and acetone. Then, 5% H₂SO₄ and 5% Na₂S₂O₈ solution were used to deoxidize. Before the substrates were introduced into the electroless plating nickel (EN) solution, they were subjected to activation in a solution containing 20 ppm PdCl₂. The electroless nickel deposition solution comprises 0.10 M nickel sulfate, 0.20 M sodium acetate, 0.04 M lactic acid 0.04 M citrate acid, and sodium hypophosphite with concentrations from 0.20 to 0.40 M at increments of 0.05 M. In addition, to ensure ultralow phosphorus content in the alloy, 0.1 M ethylenediamine was added to the EN solution when the hypophosphite sodium concentration was 0.20 and 0.25 M. The design of experimental method was described in our previous reports. All chemicals are analytical grade. Solutions were prepared by Milli-Q ultrapure water with a resistance of 18 MΩ or higher. The pH value of the solution was adjusted with KOH to 5.5. The reaction temperature of EN solution was maintained at 85 ± 2 °C.

2.2. Structure and Composition Analysis. The field-emission scanning electron microscope (FE-SEM) images were obtained on a JSM-6330F scanning electron microscope (JEOL Ltd.). The elemental composition in samples was determined with an energy dispersive X-ray spectrometer (EDS) on a Link-ISIS-300 (Oxford Corp.).

2.3. Electrochemical Measurement. EIS measurements were performed on an electrochemical workstation model ref. 600 (Gamry Inc.) in a conventional three-compartment Pyrex cell. An ac voltage (sine wave) with an amplitude of 10 mV was used as the imposing signal, and the measurement frequency range was set from 10 000 to 0.01 Hz. A defined sample area of 1.0 cm² was exposed to the electrolyte. A Luggin capillary was placed near the working electrode to minimize ohmic drop. A saturated calomel electrode (SCE) and a platinum sheet were used as the reference and counter electrodes, respectively. All electrode potentials are referenced to SCE. All the EIS measurements were conducted at open-circuit potential, Ecorr.

In order to study H⁺ corrosion, the working electrode was dipped into a 0.20 M HCl and 0.14 M citric acid solution. In the case of Au³⁺ corrosion, electrolyte comprises 0.01 M HAuCl₄, 0.14 M citric acid, and 0.04 M HCl. The temperature during experiments was maintained at 25 ± 2 °C.

2.4. Theoretical Calculation Methods. The computations reported were carried out with the Gaussian 03 code, employing the hybrid Becke exchange and Lee, Yang, and Parr correlation (B3LYP) density functional method. For hydrogen, oxygen, chlorine, and phosphorus, 6-311G(d,p) basis sets were used in this work. The effective core potential (ECP) of LANL2DZ basis sets was adopted by Hay and Wadt for the nickel and gold atoms. Those basis sets have also been used to study the mechanism of electroless and electrodeposition by Homma and Bozzini. The molecular geometry and natural bond orbital (NBO) of all species were calculated to study the corrosion behavior of CNi–P alloy.
3. RESULTS AND DISCUSSIONS

3.1. Structural and Electronic Properties of the Ni$_9$P$_x$ Cluster. The optimized structures and NBO properties for Ni$_9$, Ni$_9$P$_2$, and Ni$_9$P$_4$ clusters were described in Figure 2. Compared to nickel atoms, phosphorus atoms have a stronger electron attractive capability. For the first layer atoms, the charge of the nickel atoms increased from 0.001 for Ni$_9$ to 0.116 for Ni$_9$P$_2$ and Ni$_9$P$_4$. The excessive electronic density was caught by adjacent phosphorus atoms, which led to a varying change from $-0.318$ (in Ni$_9$P$_2$) to $-0.304$ (in Ni$_9$P$_4$). Obviously, the doped phosphorus atoms are able to bind free electrons in Ni$\hspace{1mm}$P alloy.

The electron binding effect of phosphorus can also be proved through electrostatic potential analysis of Ni$_9$P$_{0-4}$ clusters, as shown in Figure 3. The negative charge area is at the centers surrounding the phosphorus atoms, as shown in the top and side face of the Ni$_9$P$_x$ clusters. Additionally, the electrostatic intensity bar increases from $-1.342e^{-2}$ (in Ni$_9$) to $-1.611e^{-2}$ (in Ni$_9$P$_2$) and then to $-2.477e^{-2}$ (in Ni$_9$P$_4$).

As a matter of fact, Ni$_3$P clusters are the most stable nickel/phosphorus compound. Those clusters exist on the boundary of Ni$_9$P$_2$ and Ni$_9$P$_4$ clusters (Figure 2). The Ni$_3$P microcrystal has been measured by the XRD pattern in prior research, especially in Ni$\hspace{1mm}$P alloy after heat treatment.

3.2. Structure and Composition of Ni$\hspace{1mm}$P Alloy Samples. The SEM images of the EN films on pure copper surfaces are shown in Figure 4. The sample order from panel a to e corresponds to a progressively increasing phosphorus content in the Ni$\hspace{1mm}$P alloys from 6.4 to 22.3 atom %. Regarding the defects observed at the crystal boundaries, both ENe and ENd are less obvious than others. The density of defects on the alloy surface decreases with an increase of phosphorus content. In addition to the possible compromise to the mechanical property of the EN alloy, these crystal boundary defects are likely to result in overetching.

3.3. Corrosion Behavior of the Ni$\hspace{1mm}$P Alloy in Acidic Electrolyte. In the EIS measurement of EN samples dipped in H$^+$-containing solution, a single ellipse circle was observed in the Nyquist plot, as shown in Figure 5a. This means there is only one time constant in the process, which corresponds to a charge–discharge process in the electric double layer. The EIS data is
equivalent to an electric circuit, in which a solution resistance ($R_s$) is in series with a parallel connection of the constant phase element (CPE) and polarization resistance ($R_p$) (Figure 5c). $R_s$ resulted from electrolyte resistance. The CPE is due to a surface irregularity of the electrode, which can be considered as a pseudocapacitance when the value of $n$ approaches 1.0 in our experiments. The characteristic and analytical method of CPE in the Nyquist plot is described in previous literature.4 Because of a single time constant in the Nyquist plot, corrosion resistance is directly relative to the value of $R_p$. The higher $R_p$ value suggests larger corrosion resistance.

The simulation results indicate that the $R_p$ values progressively increase from 88.49 (ENa) to 6703.03 (ENe) Ω·cm$^2$ in acidic electrolyte with an increase in phosphorus content in the Ni–P coating. The corrosion resistance measured with the low-phosphorus EN alloys is much smaller than that of pure nickel (2809.8 Ω·cm$^2$) as shown in Figure 5a. As plots of ENa and ENb are hardly described in Figure 5a because of the small value of $R_p$, these two plots are enlarged and described in Figure 5b. The corrosion resistance increased with the phosphorus content in the Ni–P layers, although insufficient phosphorus doping led to more serious corrosion. An irreversible capacitive loop in the Nyquist plots for ENa and ENb samples were observed and are shown in Figure 5b. The ellipse circles transferred to oblique parabolas in the plots, perhaps because of a change in corrosion behavior in the low-frequency range. This transition relates to some irreversible reactions such as the excessive corrosion of EN alloy occurring at the interface of the electrode and electrolyte. These results suggest that an aggressive corrosion is very likely on the ENa and ENb film surface. A detailed analysis for the irreversible capacitive loop was discussed in our previous paper.19

The optimized structures and NBO properties for Ni$_9$P$_0$–4·2HCl·2H$_2$O are described in Figure 6. Considering the solvent effect, two water molecules were added to the model. In the corrosion of nickel in HCl solution, hydrogen ions are oxidative species, which can obtain electrons from nickel atoms, and eventually are reduced to atomic hydrogen. When the substrate is the Ni$_9$ cluster (Figure 6a), there is a preference for hydrogen ions to adsorb on the nickel atom surface. However, the preference will change to phosphorus atoms (Figure 6b and 6c) when phosphorus atoms dope the alloys.

Figure 5. Nyquist plots for EN samples in 0.2 M HCl electrolyte (a). Enlarged plots for ENa and ENb (b), and an equivalent circuit model for EIS simulation (c).

Figure 6. Optimized geometries and NBO charge distribution for (a) Ni$_9$, (b) Ni$_9$P$_2$, and (c) Ni$_9$P$_4$ clusters in 2(H$_2$O+HCl) electrolyte.
During the metallic corrosion process, when the metal atoms change to metallic ions, the positive charge of the metal atoms will increase. The higher positive charge means a lower corrosion resistance. The positive charge of the nickel atoms on the top layer decreased from 0.311 (Ni₉), 0.242 (Ni₉P₂) to 0.119 (Ni₉P₄). The results show that corrosion resistance of EN films in HCl solution can be improved from the doping of phosphorus atoms in the alloys.

Obviously, there exists a strong interaction between hydrogen ions and doped phosphorus atoms. In addition, the Ni–Cl bond is lengthened from 2.235 to 2.265 and then to 2.518 Å, depending on the amount of phosphorus doping. This lengthening shows that the doped phosphorus atoms can decrease the complex formation strength between the nickel and chlorine atoms and preclude the corrosion resulting from specific adsorption of chlorine ion.

In order to study the possible interaction between H₂O⁺ and Ni–P alloy, the molecular orbitals of H₂O⁺ and Ni₉P₀–₄ clusters are described in Figure 7. There exists a stronger π electron on the delocalization region (Ni–Ni) in the Ni₉ cluster. The π electron structure is broken when phosphorus atoms are doped. This leads to a decrease of the (Ni–Ni) region from four (Ni₉) to none (Ni₉P₄) on the first atom layer. The free electron density is centered on the phosphorus atoms, as shown in Figure 2.

As the energy difference between molecular orbitals will be as low as possible, the HOMO energy difference between the Ni₉P₀–₄ cluster and its compounds decrease from 0.033 to 0.018 and 0.011 hartree with an increase of phosphorus atoms (Figure 7). This indicates that doped phosphorus atoms are helpful to improve specific adsorption of H₂O⁺ on the Ni₉P₀–₄ cluster. Generally, H₂O⁺ easily adsors on the rich electron density region because of its electron-deficient ion.

These calculations and analyses illustrate that the doped phosphorus atoms become negative charge centers, by bonding the free electrons from nickel atoms. As a result, H₂O⁺ is prone to adsorb on the phosphorus atoms because of their higher negative charge. However, phosphorus atoms cannot provide electrons to H₂O⁺. Thus, the corrosion cannot occur on the high phosphorus-content Ni–P alloy surface, although a stronger interaction exists between it and H₂O⁺.

3.4. Corrosion Behavior of Ni–P Alloy in Acidic Electrolyte Containing Au³⁺ Ions. The corrosion behaviors of Ni–P alloy films in acidic HAuCl₄ solution were analyzed by EIS measurements (Figure 8). The results indicate that Ni–P alloys with higher phosphorus content are able to inhibit Au³⁺ corrosion. The values of Rₑ increase from 42.7 Ω·cm² (ENa) to 6790 Ω·cm² (ENe). There are three irreversible capacitive loops in all Nyquist plots (Figure 8a). The plots for ENa and ENb are also enlarged in Figure 8b. This indicates that serious corrosion occurs on the Ni–P alloy with lower phosphorus content. This conclusion is consistent with the corrosion behavior of Ni–P alloy in H₂O⁺ electrolyte (Figure 5).

Compared to corrosion of Ni–P in H₂O⁺, Au³⁺ can lead to more aggressive corrosion, and a much lower Rₑ value was measured with Au³⁺ solution relative to H₂O⁺ solution. The Rₑ obtained from the ENc sample decreases from 4008 (in H₂O⁺) to 2965 (in Au³⁺) Ω·cm². In the case of pure nickel, the Rₑ decreases from 2809.8 (in H₂O⁺) to 736.9 (in Au³⁺) Ω·cm².

The optimized structure and the NBO charge distribution of Ni₉P₀–₄ clusters in HAuCl₄ electrolyte are described in Figure 9. The highest positive charge of the nickel atom decreases from 0.399 (Ni₉) to 0.236 (Ni₉P₂) and then to 0.198 (Ni₉P₄) with an increase in the amount of phosphorus. In the meantime, the charge of the gold atom increases from −0.194 (Ni₉) to 0.374 (Ni₉P₄) and then to 0.456 (Ni₉P₄). These results indicate that corrosion resistance gradually increases with doped phosphorus. Au³⁺ ions nearly cannot obtain free electrons from the Ni–P alloy because of a bonding electron effect derived from the phosphorus atoms. Thus, the doped phosphorus atoms are...
capable of inhibiting excessive corrosion of the Ni–P alloy in Au\textsuperscript{3+} ion-containing acidic solution. As a result, the Ni–P films with high content of doped phosphorus are able to avoid “black pad” corrosion failure for the ENIG process in PCB applications.

As the energy difference between the molecular orbital generally is low, the energy difference of the HOMO orbital for Ni\textsubscript{9}P\textsubscript{0.4} clusters and (Ni\textsubscript{9}P\textsubscript{0.4}+HAuCl\textsubscript{4}) compounds decrease from 0.058, 0.020 to 0.019 hartree when the content of doped phosphorus atoms increases from 18.2 atom % to 30.8 atom % (Figure 10). Obviously, there is a stronger interaction between the Au\textsuperscript{3+} ion and Ni\textsubscript{9}P\textsubscript{4} cluster, relative to others. Also, the charge of the nickel atom in the (Ni–Au–P) region decreases from 0.236 for Ni\textsubscript{9}P\textsubscript{2} to 0.123 for Ni\textsubscript{9}P\textsubscript{4} clusters (Figure 9). The doped phosphorus atoms are able to bond free electrons near the nickel atoms and then exhibit electronegativity. Although H\textsuperscript{+} or Au\textsuperscript{3+} ions specifically adsorb on the doped phosphorus atoms, these cations cannot obtain electrons.

3.5. Optimal Phosphorus Doping Content for ENIG. In this work, our purpose is to optimize the phosphorus content in Ni–P alloys for the ENIG process and mitigate the excessive corrosion “black pad” failure in the immersion gold process. It was found that the Ni–P alloy with below 6.0 wt % phosphorus content cannot meet the demand of Au\textsuperscript{3+} ion corrosion. On the other hand, if the corrosion degree is insufficient in the Au\textsuperscript{3+} solution, nickel atoms cannot be replaced by gold atoms to meet the requirement of ENIG in PCB manufacture. Experimental measurement once indicated that no replacement reaction between Au\textsuperscript{3+} ions and Ni atoms could occur when corrosion

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**Figure 9.** Optimized geometries and NBO charge distribution for (a) Ni\textsubscript{9}, (b) Ni\textsubscript{9}P\textsubscript{2}, and (c) Ni\textsubscript{9}P\textsubscript{4} clusters in HAuCl\textsubscript{4}+2H\textsubscript{2}O electrolyte.

**Figure 10.** Molecular orbital LUMO of Au\textsuperscript{3+}, HOMO of Ni\textsubscript{9}P\textsubscript{0.4} clusters, and (Ni\textsubscript{9}P\textsubscript{0.4}+HAuCl\textsubscript{4}) compounds and their corresponding energies.

**Figure 11.** Relationship of corrosion impedance (R\textsubscript{p}) and doped phosphorus amount (atom % and wt %). The content of doped phosphorus fitting for the ENIG process is marked by thin grid lines.
The corrosion behavior of Ni–P alloys was investigated in H⁺ and Au³⁺ cation-containing solutions as a function of doped phosphorus content through a combination of theoretical and electrochemical methods. The relevant results and discussion propose a possible mechanism whereby corrosion resistance of Ni–P alloys can be enhanced with doped phosphorus content. As the doped phosphorus atoms are able to bond free electrons around nickel atoms, the crystal structure of Ni–P alloys change from metallic to the amorphous state, which makes phosphorus atoms exhibit electronegativity. Also, the alloys that form metallic glass with high phosphorus content will have less free electrons. This doped phosphorus can attract oxidative cations such as H⁺ and Au⁺ but cannot provide electrons to them. The effect is beneficial for enhancing corrosion resistance of Ni–P alloys. The DFT calculation results also suggest a possible mechanism to explain corrosion behaviors of Ni–P alloys in different electrolytes. Based on the theoretical and experimental results, an optimal phosphorus content in Ni–P alloys ranging from 6.0 to 9.0 wt % is proposed for the application of the immersion gold process in PCB manufacture.

4. CONCLUSION

The corrosion behavior of Ni–P alloys was investigated in H⁺ and Au³⁺ cation-containing solutions as a function of doped phosphorus content through a combination of theoretical and electrochemical methods. The relevant results and discussion propose a possible mechanism whereby corrosion resistance of Ni–P alloys can be enhanced with doped phosphorus content. As the doped phosphorus atoms are able to bond free electrons around nickel atoms, the crystal structure of Ni–P alloys change from metallic to the amorphous state, which makes phosphorus atoms exhibit electronegativity. Also, the alloys that form metallic glass with high phosphorus content will have less free electrons. This doped phosphorus can attract oxidative cations such as H⁺ and Au⁺ but cannot provide electrons to them. The effect is beneficial for enhancing corrosion resistance of Ni–P alloys. The DFT calculation results also suggest a possible mechanism to explain corrosion behaviors of Ni–P alloys in different electrolytes. Based on the theoretical and experimental results, an optimal phosphorus content in Ni–P alloys ranging from 6.0 to 9.0 wt % is proposed for the application of the immersion gold process in PCB manufacture.

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