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Evaluation of the Mechanical Properties of Multi-nano Layered Copper-Nickel Thin Film by the Dynamic-Nano Indentation Method

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The dynamic nano-indentation method was applied to study the effect of interface moving behavior with heat treatment on the nano-mechanical properties of multi-nano-layered copper-nickel thin film. Layer-by-layer depositions of copper and nickel of nano-sized thickness were prepared by two-step pulse electro-deposition in a modified copper-nickel sulfate bath at 25°C. The multi-layered copper-nickel thin sheet was composed of a 20-nm-thick copper-rich nickel phase, and a 25-nm-thick nickel-rich copper phase. Thermal vacuum annealing influenced the interface morphology between copper and nickel nano-layers. Inter-diffusion mainly occurred after annealing at 500°C for 6 h. The interface disappeared after annealing at 600°C to form a completely solid solution. Thermal annealing reduced the nano-hardness and elastic recovery. The average nano-hardness of the multi-layered nano-copper-nickel thin film for the specimens of as-received, 300°C, 500°C and 600°C were 7.9 Gpa, 6.1 Gpa, 4.7 Gpa and 3.0 GPa, respectively. The elastic stiffness was 15.77×10^4 Nm^{-1} for the as-received specimen, which finally became 2.98×10^4 Nm^{-1} for the specimen after annealing at 600°C for 6 h.

INTRODUCTION

Multi-layered copper and nickel thin film has received attention in materials research and applications because it is a well-known inter-diffusion couple with a high electromagnetic interference (EMI) shielding properties.[1,2] The copper-nickel thin film can be prepared by several methods, including vacuum deposition, cladding, and electro-deposition.[3] Inter-diffusion at the interface of the copper and nickel film during annealing causes material degradation by interface grooving and microstructure variation.[4] The inter-diffusion behavior depends on the metallurgical parameters, like grain boundary and vacancy concentration. Since the electro-plating should introduce columnar grains with atomic-sized defects due to hydrogen gas evolution and relatively high residual stress, the inter-diffusion behavior of the copper and nickel layer formed by electro-plating is different from that of conventional copper-nickel diffusion couples.[2,5] The atomic-sized defects due to hydrogen gas evolution can be evaluated by small-angle neutron scattering.[6] The residual stress of the electro-deposited copper-nickel layers is actually difficult to evaluate. The residual stress change can be analyzed by precise measurement of local mechanical properties because a stress-relief heat treatment can remove the residual stress.[7]

Recently, a dynamic nano-indentation method was introduced to analyze the mechanical properties of various thin films.[8,9] Although many studies of nano-mechanical properties of thin film have been carried out, little information is available about electroplated thin film, especially multi-layered thin film.[10,11] Hence, the objectives of this study were to prepare multi-layered nano-copper and nickel thin film by electro-deposition and to apply a dynamic nano-indentation method to study the effect of inter-diffusion on the multi-nano-layered thin film by in situ measurement of the nano-mechanical properties with annealing.

EXPERIMENTAL METHOD

The multi-layered nano-copper and nickel thin film was prepared by electro-deposition in a copper-nickel sulfate bath. Table I shows the composition of

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the electroplating bath for the multi-layered copper-nickel deposition. The electro-plating solution was prepared by dissolving $CuSO_4{\cdot}5H_2O$ (>99.0%, Samchun, Korea), $NiSO_4{\cdot}6H_2O$ (>98.5%, Samchun), and $Na_3C_6H_5O_7{\cdot}2H_2O$ (>99.0%; Sigma Aldrich, USA) with adequate weight ratio into distilled water. The pH was controlled with H_2SO_4 and NH_4OH. The electroplating was carried out at 25°C by a two-step pulse plating method (Jisan 300; Korea).

The microstructure and chemical composition were observed by transmission electron microscopy (TEM; JTM-2010; Jeol, Japan), and energy dispersive spectroscopy (EDS; Oxford, UK). The specimens for TEM work were prepared by focused ion beam (Auriga, Zeiss, Germany). The mechanical properties of the thin film were determined by the dynamic nano-indentation method (TI 750; Hysitron, USA) at a load of 10^4 μN and interval of 7 μm, with a vacuum heating unit (T-100; R & B, Korea). Figure 1 is a schematic diagram of the in situ nano-indentation test system with a hot plate and vacuum annealing chamber. Figures 2 and 3 are photos of the in situ nano-indentation test with the heating unit and the vacuum annealing system, respectively.

RESULTS AND DISCUSSION

Chemical Composition and Microstructure

Figure 4 shows a TEM image and its chemical mapping of the multi-layered nano-copper and nickel thin film formed by electro-deposition on a copper substrate. The figure shows that the thin film with nano-thicknesses of copper and nickel layers was well formed by the pulse electroplating under the conditions of -0.2 V_{SHE}, -0.05 Am^{-2}, and 25 s for copper deposition, and -1.7 V_{SHE}, -0.5 Am^{-2}, and 80 s for nickel deposition, at pH = 1.0 and 25°C. The multi-nano layers were composed of the copper-rich phase of about 20 nm in thickness, and the nickel rich phase of about 25 nm in thickness, respectively. Figures 5, 6, and 7 are TEM images and their chemical mappings of the multi-nano-layered copper and nickel thin film after vacuum annealing at 300°C, 500°C and 600°C for 6 h, respectively. Figure 5 shows that the interface morphology between the copper and nickel nano-layers was similar to that of as-received specimen. However, Fig. 6 shows that the interface morphology after annealing at 500°C tended to be grooved due to inter-diffusion, which disappeared after annealing at 600°C, and formed a completely solid solution, as shown in Fig. 7.

Nano-mechanical Properties

The nano-mechanical properties of the multi-nano-layered copper-nickel thin film were determined by the dynamic nano-indentation method

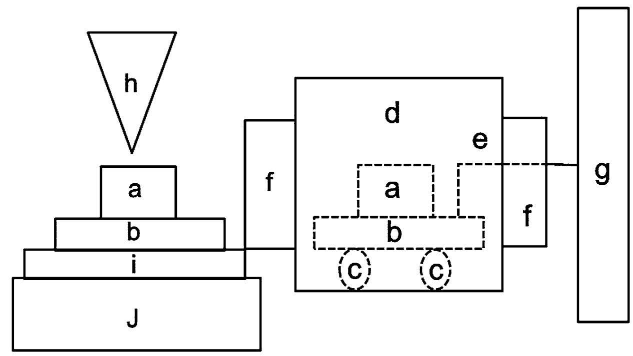

Fig. 1. A schematic diagram of in situ nano-indentation test with a heating unit and vacuum annealing system: (a) specimen, (b) hot plate, (c) moving stage, (d) vacuum chamber, (e) thermocouples and heating wires,(f) gate, (g) controller, (h) nano-indenter, (i) insulation board, (j) indenter stage.

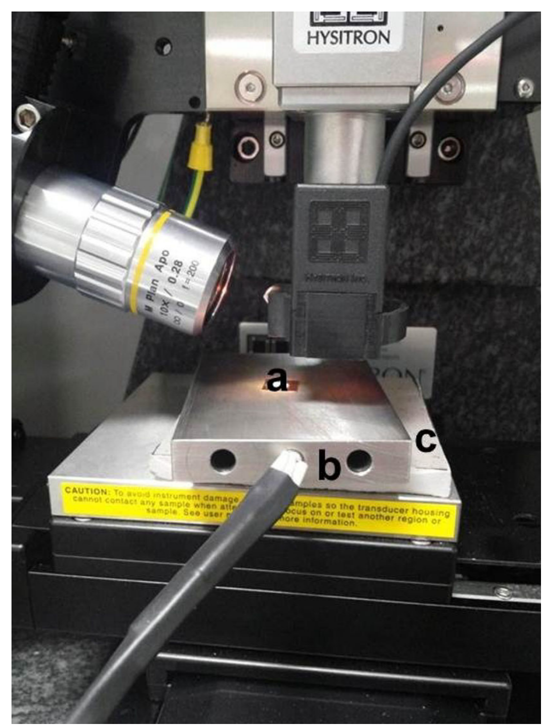

Fig. 2. In situ nano-indentation test with a heating unit: (a) specimen, (b) hot plate with thermocouples, (c) insulation board.

Table I. Chemistry of the electroplating solution for multi-nano-layered copper-nickel (wt.%)

$NiSO_4{\cdot}6H_2O$	$CuSO_4{\cdot}5H_2O$	$Na_3C_6H_5O_7{\cdot}2H_2O$	H_2O
14.62	0.08	5.84	79.46

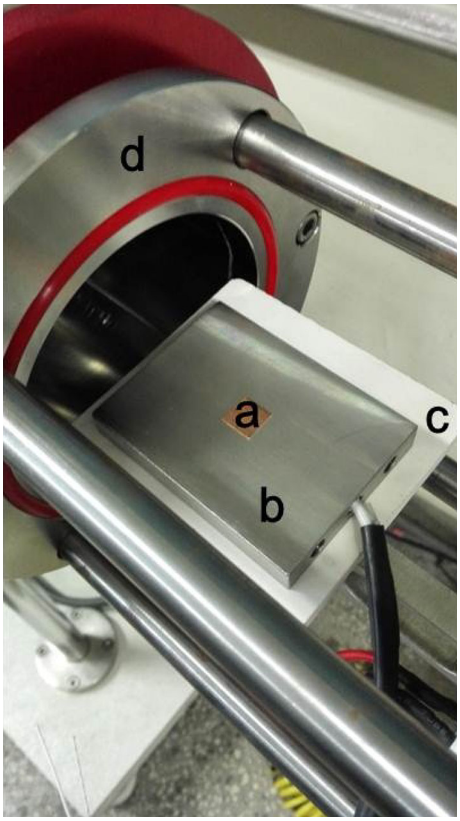

Fig. 3. A vacuum annealing chamber attached on an in situ nanoindentation test with a heating unit: (a) specimen, (b) hot plate with thermocouples, (c) moving stage with insulation board, (d) vacuum chamber.

because the annealing resulted in inter-diffusion occurring at the interface between the copper and nickel layers, and also the removal of residual stress due to electro-plating.[9] Figure 8 shows typical cyclic load–time–displacement curves of the multi-nano-layered nano-copper-nickel thin film with various annealing temperatures. The figure also shows the variation of elastic stiffness and elastic recovery in the load–time–displacement with annealing. The elastic stiffness determined by the slope was 15.77×10^4 Nm^{-1} for the as-received specimen, which tended to be slightly reduced with annealing and finally became 2.98×10^4 Nm^{-1} for the specimen after annealing at 600°C for 6 h, whereas the elastic recovery after final unloading reduced with annealing. The average nano-hardnesses of the multi-nano-layered copper-nickel thin film formed by electro-deposition for the as-received specimens at 300°C, 500°C and 600°C were 7.9 Gpa, 6.1 GPa, 4.7 GPa and 3.0 GPa, respectively. Several metallurgical factors that affect hardening and softening decided the final nano-hardenss of the electroformed layer. Among them, the annealing above 300°C acts to remove residual stress of the layer, and reduces nano-hardness, whereas inter-diffusion

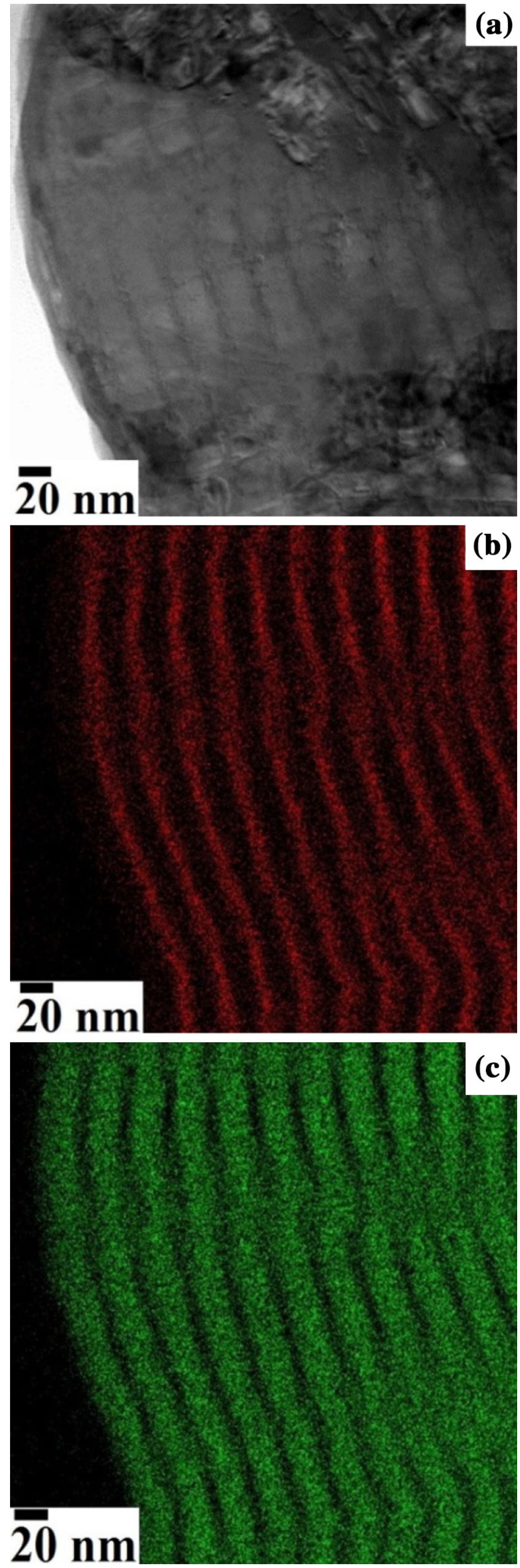

Fig. 4. TEM images and EDX mapping of the multi-nano-layered copper-nickel thin film formed by pulse plating: (a) TEM image, (b) Cu, (c) Ni.

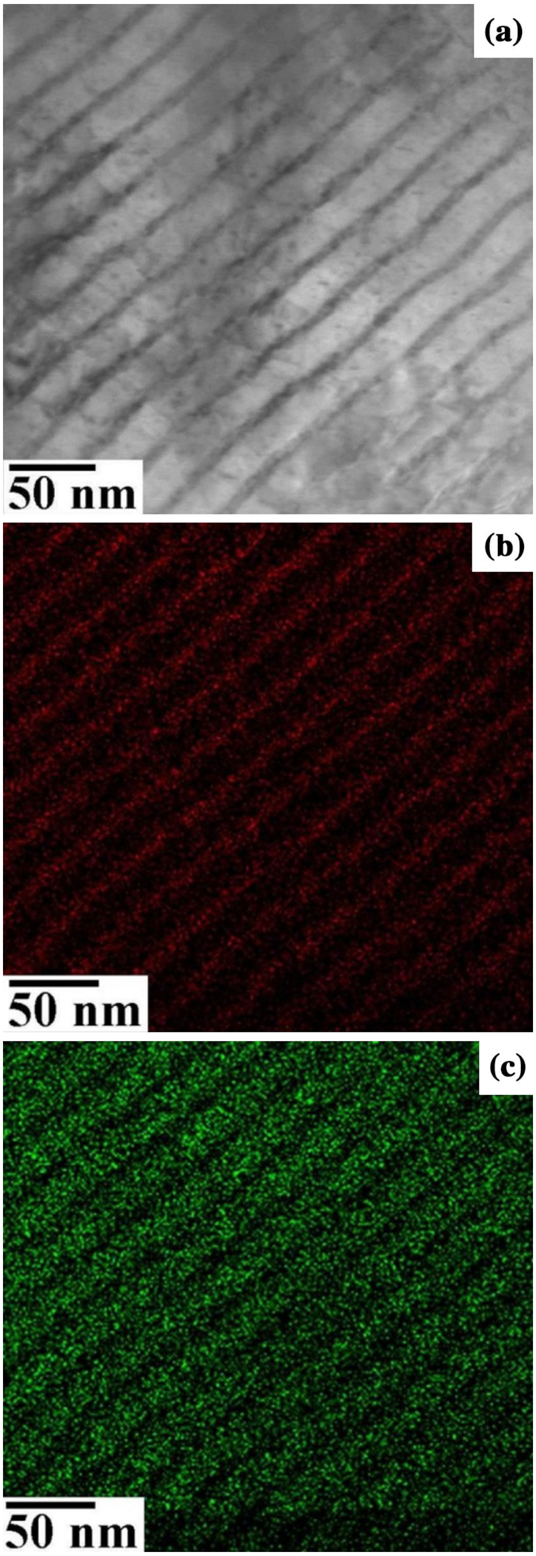

Fig. 5. TEM images and EDX mapping of the multi-nano-layered copper-nickel thin film after vacuum annealing at 300°C for 6 h: (a) TEM image, (b) Cu, (c) Ni.

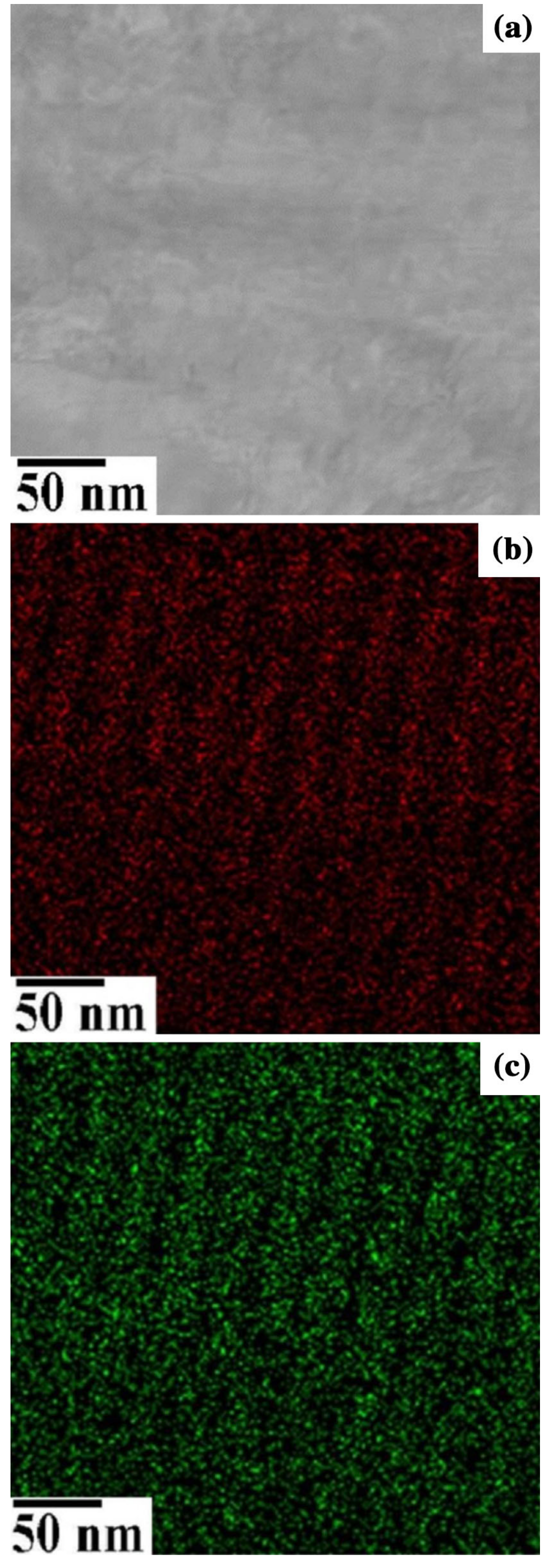

Fig. 6. TEM images and EDX mapping of the multi-nano,layered copper-nickel thin film after vacuum annealing at 500°C for 6 h: (a) TEM image, (b) Cu, (c) Ni.

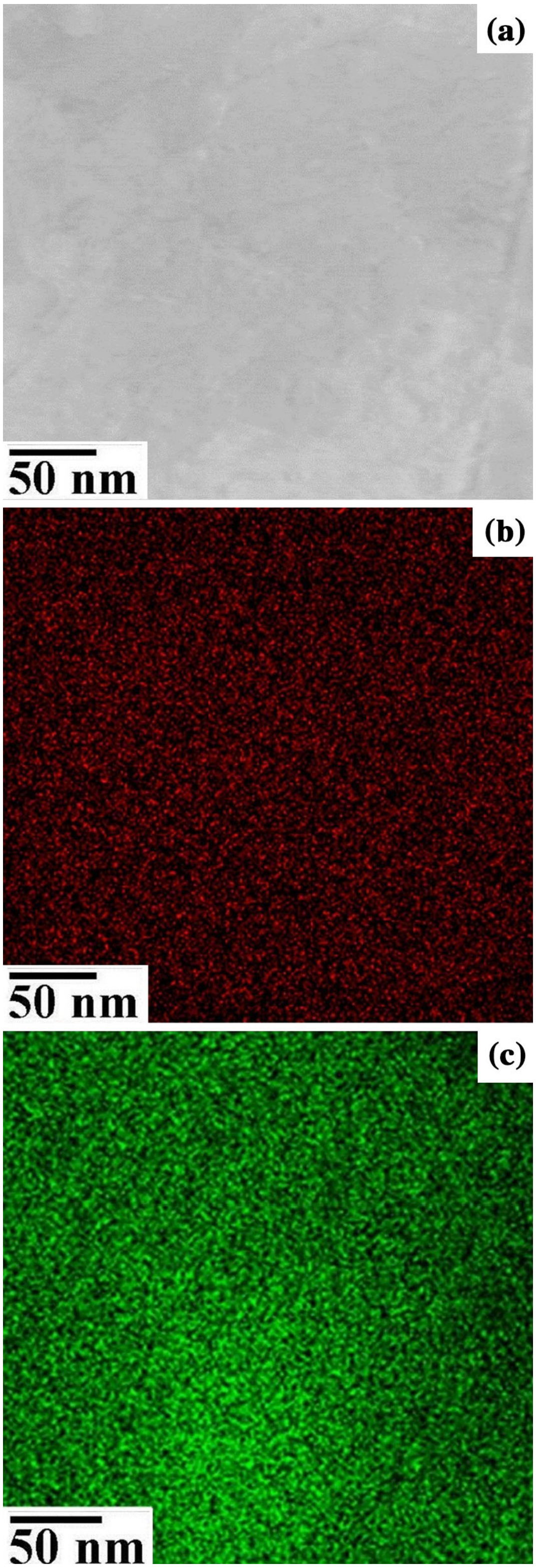

Fig. 7. TEM images and EDX mapping of the multi-nano-layered copper-nickel thin film after vacuum annealing at 600°C for 6 h: (a) TEM image, (b) Cu, (c) Ni.

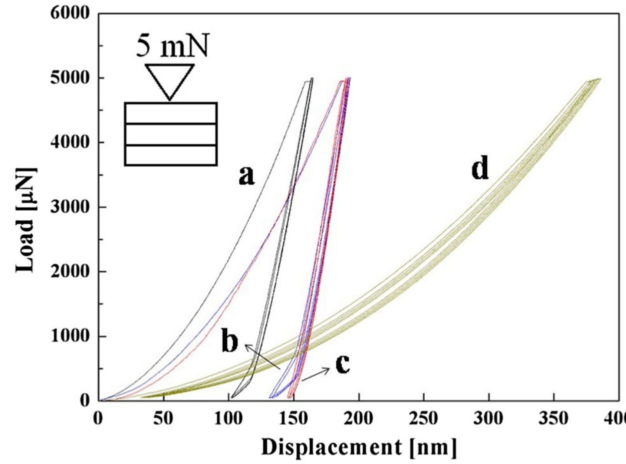

Fig. 8. Typical cyclic load-time-displacement curves of electro-formed copper-nickel multi-nano-layered thin film with various annealing temperature for 6 h: (a) as-received, (b) 300°C, (c) 500°C, (d) 600°C.

at the interface between copper and nickel may harden a solid solution, and increase the nano-hardness. Hence, the reduction of the nano-hardness after annealing at 300°C relates to residual stress relief, and that after annealing at 600°C is not related to solid solution hardening, because the annealing at 300°C and 600°C in this study resulted in decreasing hardness and elastic recovery, respectively.

CONCLUSION

1. Multi-nano-layered copper-nickel thin film was well produced by pulse electro-plating in a modified sulfide bath. The multi-nano-layered copper-nickel thin film consisted of a copper-rich phase of about 20 nm in thickness, and a nickel rich phase of about 25 nm in thickness, which formed at the condition of $-0.2\ V_{SHE}$, $-0.05\ Am^{-2}$, and 25 s for copper deposition, and $-1.7\ V_{SHE}$, $-0.5\ Am^{-2}$ and 80 s for nickel deposition.
2. Vacuum annealing influenced the interface morphology between the copper and nickel nano-layers. The interface morphology after annealing at 300°C was little changed. After annealing at 500°C, it was grooved due to inter-diffusion. After annealing at 600°C, the interface disappeared to form a completely solid solution.
3. Thermal annealing changed the elastic stiffness and elastic recovery of the multi-nano layered copper-nickel thin film. The elastic stiffness was $15.77 \times 10^4\ Nm^{-1}$ for the as-received specimen, which finally became $2.98 \times 10^4\ Nm^{-1}$ for the specimen after annealing at 600°C for 6 h. The

elastic recovery after final unloading reduced with annealing.

4. The average nano-hardness of the multi-nano layered copper-nickel thin film formed by electro-deposition for the as-received specimens at 300°C, 500°C and 600°C were 7.9 GPa, 6.1 GPa, 4.7 GPa and 3.0 GPa, respectively. The reduction of nano-hardness after annealing at 300°C is related to residual stress relief.

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