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Efficient Electroless nickel plating from highly active Ni-B nanoparticles for electric circuit pattern on Al_2O_3 ceramic

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EXPERIAMENTAL METHOD

Synthesis of Nano-Ni/B. The Ni-B sol was prepared in a solution containing 24.0 g/l $NiCl_2 \cdot 6H_2O$, 5 g/L polyvinyl pyrrolidone (PVP), and 5 g/L cetyltrimethyl ammonium bromide (CTAB) in ethanediol agent. In a typical approach, the solution was stirred at a rate of 1000 rmp and 5.0 ± 2°C. Then, the $NaBH_4$ and ethanediol solution was slowly added into the above solution using a peristaltic pump. The mole ratio of $NaBH_4$ to $NiCl_2$ for the synthesis of Ni-B nanoparticles is 4:1, because the Ni-B nanoparticles is unstable in the solution when the mole ration is smaller than 4:1.

Analysis of the Catalytic Characteristics. Electrochemical measurements were performed in a three-electrode cell using an electrochemical workstation Model Ref. 600 (Gamry Inc. USA). The Ni-B species were applied on a glass carbon mixed with PTFE latexes, and was treated at 200 °C for 15 min. A pure nickel sheet was also used for a comparison. A platinum foil and a saturated Hg/Hg_2SO_4 electrode (SCE) were used in the experiment as the counter and reference electrodes, respectively. The pure nickel sheet being a working electrode was mechanically polished by SiC sandpaper with 600 and 1200 grade. Then, it was cleaned with ethanol and acetone. Finally, it was activated in 10.0 wt% H_2SO_4 solution. The reference electrode was protected by glass tube filled with saturated K_2SO_4 solution to avoid the possible contaminate in electrolyte.

In cyclic voltammetry (CV) experiments, the voltammograms were recorded in an anodic sweep from -1.5 V to 1.5 V at a sweep rate of 10 mV/s. The solution was constantly stirred at a

mild rate using a magnetic stirring apparatus. A solution comprised of 12.0 g/L sodium acetate, 8.0 g/L lactic acid, and 5.0 g/L citrate acid was denoted as sample A (SA) solution. Another solution containing 30.0 g/L sodium hypophosphite was refered to sample B (SB) solution. The pH value of the electrolyte was adjusted to 5.5 using KOH solution and the temperature was set to 60°C and 80 °C.

In electrochemical impedance spectroscopy (EIS), an ac voltage (sine wave) with amplitude of 10.0 mV was used as imposing signal, and the frequency range was set from 10 K to 0.005 Hz. Defined sample area of 1.0 cm^2 was exposed to the electrolyte. A Luggin capillary was placed near the working electrode to minimize the ohmic drop. All the EIS measurements were performed at the deposition potential, E_{dep}. All electrode potentials were referred to MSE, if not otherwise stated.

The solution for nickel electroless deposition was comprised of 25.0 g/L $NiSO_4 \cdot 6H_2O$, 30.0 g/L NaH_2PO_2, 12.0 g/L sodium acetate, 8.0 g/L lactic acid, and 5.0 g/L citrate acid. The pH value of the electrolyte was adjusted to 5.5 at the temperature 60 and 80 ^oC. All solution was prepared with analytical grade reagents and Millipore ultrapure water.

Electric Circuit Fabrication on CCPCB. The fabrication procedures of the circuit fabrication are described as follows. Firstly, the alumina ceramic substrate was roughened by strongly acidic solution. The solution contains 100 ml/L HF, 20 g/L NH_4F, 20 ml/L H_2SO_4, 5 g/L citric acid, and 5 g/L tartaric acid. The reaction was conducted at 85±2 ^oC for 10~20 min. Secondly, the ceramic surface is metalized after electroless nickel deposition followed by an electroplated copper film. In a typical process, the Ni-B precursor is coated on alumina substrate, and then annealed at 200 ^oC for 15 min. Then, to futher enhance the connection of Al_2O_3 and Ni-B film, the ceramic substrate was annealed at 600 ^oC. Subsequently, electroless nickel is coated on the activated alumina substrate followed by a copper electrodeposition. The solution and condition of electroless plating nickel was the same as described in EIS measurement. The electrodeposited copper coating was applied to further improve electron conductivity. The solution contained 200 g/L $CuSO_4$, 50 g/L H_2SO_4, 20 g/L K_2SO_4, and 0.10 g/L NaCl. The reaction temperature was controlled at 25±2 ^oC. The current density was 4.0 A/dm^2. Finally, the electric circuit pattern was formed by a masking layer followed by a chemical etching treatment.

Analysis of the Structure and Composition. The surface morphology of the Ni-B precursor was

characterized using atomic force microscopy (AFM). The scanning electronic microscopy (SEM) was employed to characterize alumina and metal films, performed on a JSM-6330F scanning electron microscopy (JEOL Ltd.). The crystalline structure of the nano-particles and coatings were determined using X-rays diffraction (XRD) on a Bruker D8 Advance X-rays θ~2θ apparatus with Cu Kα (15 406 Å) radiation. A four-point probe (FPP) was employed to measure the electronic conductivity of the resulting films on ceramic substrate at 300 K under atmosphere.

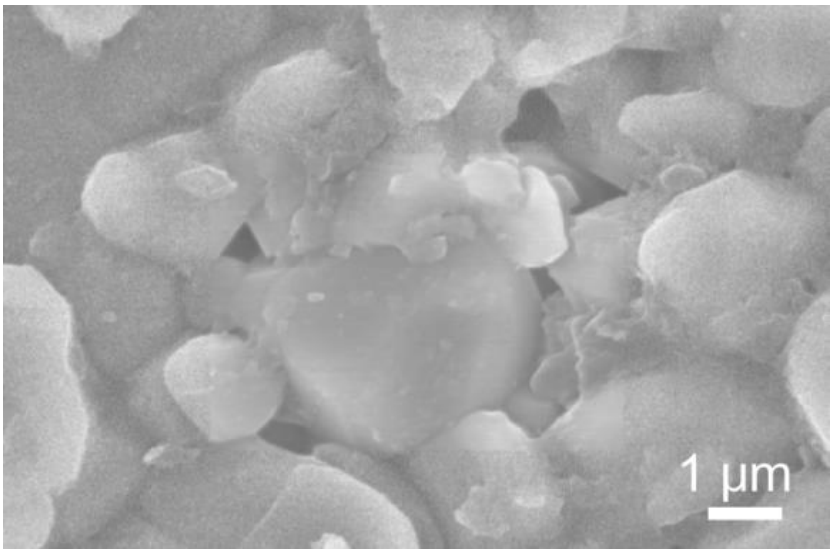

Fig. S1 SEM image of alumina ceramic substrate after roughening treatment.

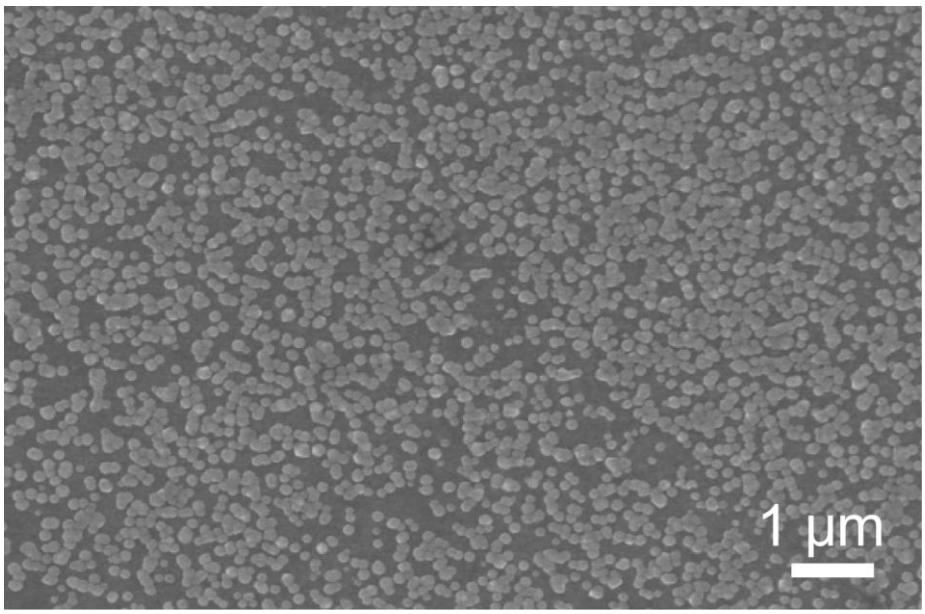

Fig. S2 SEM image of alumina ceramic substrate after ENP and then by copper electrodeposition.

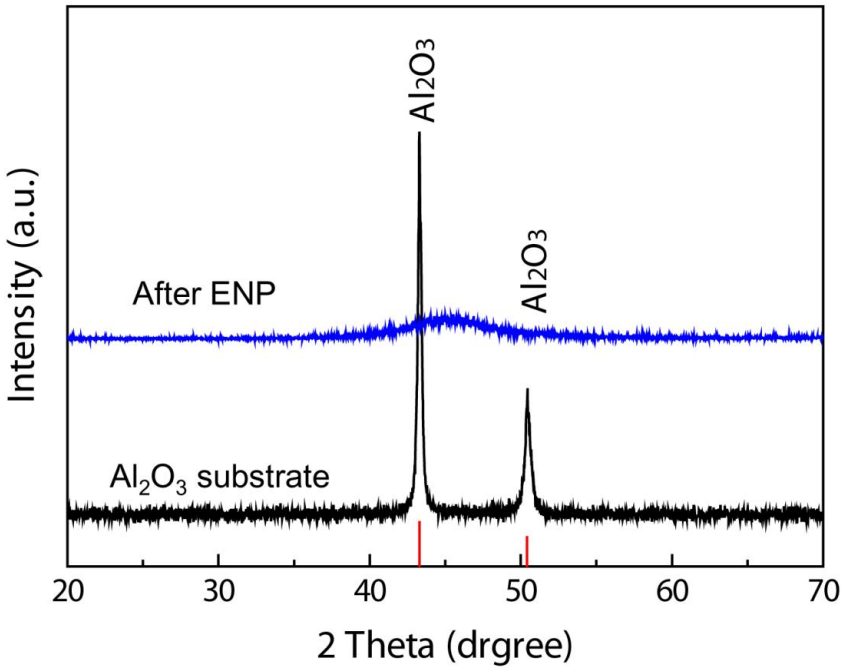

Fig. S3 XRD patterns of the alumina ceramic substrate before and after ENP.