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The electrodeposition, magnetic and electrical characterisation of Palladium–Nickel alloys

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ABSTRACT

A process for electrodepositing PdNi alloys and subsequent electrical and magnetic characterisations are reported. PdNi alloys are deposited on 0.019–0.021 Ω cm and 1–2 Ω cm n-type Silicon from a bath of Pd-ethylenediamine dichloride and Ni sulphate. Compositional analysis of films deposited at multiple deposition potentials from different bath concentrations showed that film composition can be estimated from the composition of the bath and the deposition potential used. This allows deposition of films with a range of Ni content from the same bath using different deposition potentials. The deposited films form excellent Schottky barriers on 1–2 Ω cm Si with leakage currents of the order of μA/cm^2 and a difference of about six orders of magnitude between forward and reverse bias currents. Films with Ni concentrations above 30% are observed to be ferromagnetic at room temperature and their saturation magnetisation is linearly correlated with the Ni content in the film.

1. Introduction

Palladium–Nickel (PdNi) alloys are in wide commercial use as contact materials [1] and they also form good quality contacts with electronic materials other than Silicon. Javey et al. [2] and Mann et al. [3] demonstrated reliable and good quality contacting between Pd and semiconducting as well as metallic Carbon nanotubes (CNTs). Sahoo et al. [4] formed ferromagnetic PdNi contacts to Carbon nanotubes (CNTs) to study their spintronic properties. Pure Pd [5,6] and PdNi [7] films have also been used to fabricate Hydrogen sensors by exploiting the change in electrical properties of Palladium upon absorption of gaseous Hydrogen. Pure Pd exhibits an irreversible phase change after absorption of a certain amount of gaseous Hydrogen and the addition of Ni can stabilise the sensor over a wider range of Hydrogen pressures by delaying this change. These varied examples show that Pd and PdNi alloys are quite versatile materials for use in electronics.

Kiziroglou et al. [8,9] have shown that electrodeposited Ni–Si Schottky barriers exhibit lower reverse bias currents and higher on/off current ratios compared to evaporated Ni–Si Schottky barriers. It is possible that this improvement in the contact quality be observed in PdNi–Si, PdNi–CNT and other PdNi-semiconductor systems.

The objective of this study was to investigate the possibilities of electrodepositing PdNi alloys with a wide range of Ni content and to study their magnetic and electrical properties. The experimental process and resultant data will describe the method for electrodepositing PdNi alloys, the degree of control that is possible over the composition of the alloy and its suitability for electronic and magnetic applications.

2. Electrodeposition

The recipe for the electrochemical bath used in these experiments was taken from Ref. [10] and consisted of $NiSO_4{\cdot}6H_2O$, Pd-ethylenediamine dichloride ($Pd(en)Cl_2$) and Ammonium sulphate ($(NH_4)_2SO_4$) salts with Ammonia (NH_3) as an additive and deionised(DI) water as the solvent. Solutions were prepared by varying the $NiSO_4$ concentration from 16.65 g/L to 49.95 g/L and the $Pd(en)Cl_2$ concentration from 38.85 g/L to 5.55 g/L such that the sum of the two is always 55.5 g/L. 45 mL/L of Ammonia was added during the preparation and if required, the pH was adjusted to 7–7.5 using H_2SO_4 and additional Ammonia, but the additional volumes of each were at most 0.5 mL/L. The quantity of Ammonium Sulphate was kept constant in all the solutions. The Ni content in the solution is defined as the ratio of the Ni salt concentration in g/L to that of Pd. For each Ni concentration, three solutions (Ni-only, Pd-only and PdNi) were prepared as per the values listed in Table 1, which is an example of a solution with 80% Ni content.

An n-type, ⟨100⟩ 0.019–0.021 Ω cm resistivity Si wafer was cleaved into chips of size 1.5 cm × 1 cm. The chips were washed with Acetone and Isopropylalcohol (IPA), blown dry and coated with an electrically inert varnish to prevent electrodeposition in all areas except a 1 cm × 0.5 cm window. The native Silicon oxide was etched by dipping in 20:1 HF for 15 s followed by rinsing with

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Table 1
Concentrations of components in the three solutions prepared for each combination of Ni and Pd salts. The Ni content of the solution is defined as the ratio of the Ni salt concentration to that of the Pd. This table lists the PdNi solution with 80% Ni content.

Components	Ni bath (g/L)	Pd bath (g/L)	PdNi bath (g/L)
$NiSO_4{\cdot}6H_2O$	44.40	0	44.40
$Pd(en)Cl_2$	0	11.1	11.1
$(NH_4)_2SO_4$	16.70	16.70	16.70
NH_3(35%)	45 mL/L	45 mL/L	45 mL/L

DI water. The chip was immediately immersed in the bath and electrodeposition was performed at room temperature using an Autolab PGSTAT30 system with a calomel reference electrode and Pt mesh as the counter electrode. The devices formed were used to study the composition and magnetic properties of the films.

A second set of chips from an n-type ⟨100⟩ 1–2 Ω cm resistivity Si wafer with ohmic Al backcontacts were used to fabricate and study the electrical characteristics of the PdNi–Si Schottky barriers. A 20 nm thermal oxide was grown and patterned to form sets of circular and square contacts with sizes ranging from 1.5 mm to 0.2 mm. This thermal oxide was used as a mask to restrict metal electrodeposition to patterned areas of the chip, forming the metal contacts of the Schottky barriers.

At the onset, cyclic voltammetry (CV) curves were measured for the Ni and Pd solutions by sweeping the electrode potential from 0 to −3 V and back at a while measuring the current in the electrochemical cell. All cyclic voltammetry measurements in this study were performed using a scan rate of 100 mV/s. An example of such curves is shown in Fig. 1. Currents during the reverse sweep are usually larger than the forward sweep, signifying the formation of a base metal layer, lowering of sample resistance and an increase in deposition rates for subsequent layers. Fig. 2 shows an enlarged view of the forward sweep of cyclic voltammetry curves with sharp increases in current that signify the start of Ni and Pd deposition at −0.8 V and −1.2 V respectively. From Fig. 2, it is possible to extract the currents in the Ni-only and Pd-only baths at the

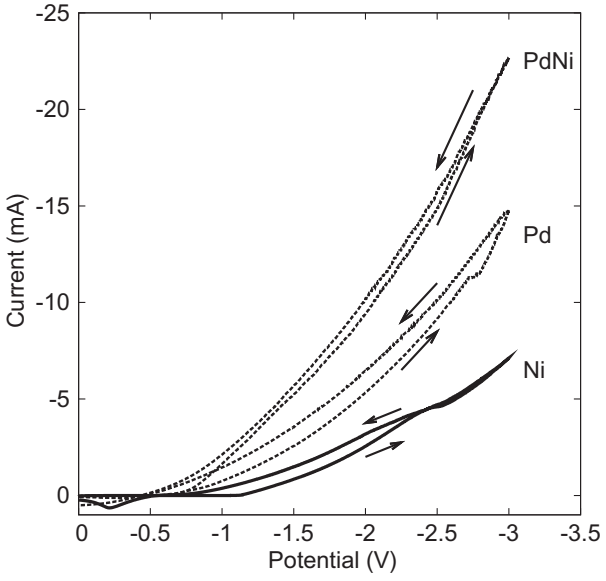

Fig. 1. Cyclic voltammetry curves for 16.65 g/L Ni-only, 38.85 g/L Pd-only and PdNi baths. The PdNi bath has the same Ni and Pd concentrations as the individual baths. The current levels are higher during the reverse sweep due to formation of a metal layer during the forward sweep. The scan rate is 100 mV/s.

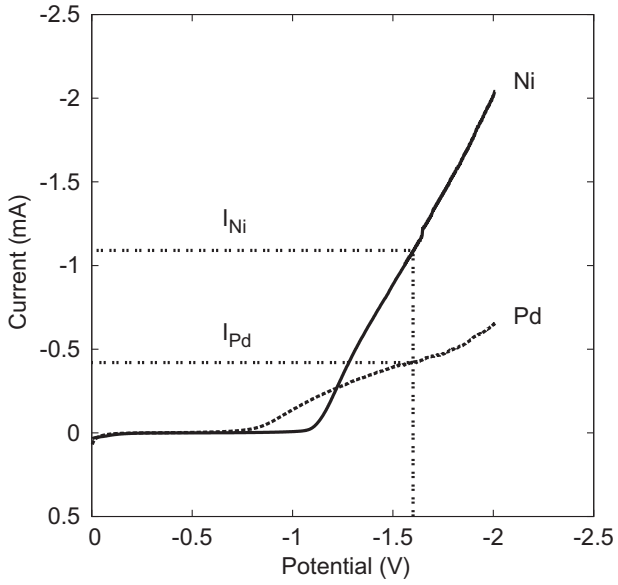

Fig. 2. Enlarged view of the cyclic voltammetry curves for 49.95 g/L Ni-only and 5.55 g/L Pd-only baths between 0 and −2 V. The method used to extract the current levels in the Ni-only and Pd-only baths at a particular potential is illustrated. These values were used to calculate the nominal film composition.

deposition potential used to deposit a PdNi film from the PdNi bath. PdNi films were deposited by immersing the sample in the PdNi bath, applying a few (1–3) high negative potential (−2.5 V) pulses for a short duration (0.1 s) and then applying a constant potential chosen such that the current density was between 1 and 3 mA/cm^2. The charge deposited during electrodeposition was measured and can be used to calculate the mass of deposited material. The high potential pulses promote formation of metal islands on the Si surface and it can be seen from SEM images in Fig. 3 that pulse potentials of −2.5 V were significantly more effective in forming metal islands compared to less negative potentials.

The presence of these metal nuclei improves film adhesion by serving as anchors between the film and the Silicon surface. The current density range of 1–3 mA/cm^2 was chosen because it yields better quality films compared to higher current ranges, where films tended to be less adherent and occasionally powdery and brittle. This is possibly due to increased Hydrogen evolution and fixation in the film at high current densities, creating internal stresses that adversely affect film quality [1]. Films deposited at lower current densities tended to be discontinuous and were therefore not suitable for use as devices. In all cases, however, films with thickness above 100 nm suffered from poor adhesion and tended to peel off or crack. After electrodeposition, the samples were washed with DI water, blown dry and characterised using Energy Dispersive X-Ray (EDX) analysis, Vibrating Sample Magnetometry (VSM) and electrical measurements.

3. Compositional analysis

The composition of the electrodeposited films was studied using a Jeol 6500 EDX system. For each sample, EDX data was acquired at multiple locations, the mean Ni and Pd atomic percentages were calculated and normalised to 100% by ignoring the EDX peak from the Si substrate. This EDX measured value was compared to the nominal Ni percentage computed using the formula

$$\mathrm{Ni}_{\mathrm{Nominal}} = I_{\mathrm{Ni}}/(I_{\mathrm{Ni}} + I_{\mathrm{Pd}}) \quad (1)$$