

Gas Phase Fabrication of Pd-Ni Nanoparticle Arrays for Hydrogen Sensor Applications

Xing Peng^{1,a}, Hongwei Zhang^{1,b}, Ling Sun^{1,c}, Fei Liu^{2,d}

¹ Department of Materials Science and Engineering, Nanjing University, Nanjing 210093, China

² Suzhou SinoRaybo Nanoscience and Nanotech Co., Ltd, Suzhou Industrial Park, 215123, Suzhou, Jiangsu, China

Abstract. Pd-Ni nanoparticles have been fabricated by gas aggregation process. The formation of Pd-Ni nano-alloys was confirmed by X-ray photoelectron spectroscopy measurements. By depositing Pd-Ni nanoparticles on the interdigital electrodes, quantum conductance-based hydrogen sensors were fabricated. The Ni content in the nanoparticle showed an obvious effect on the hydrogen response behavior corresponding to the conductance change of the nanoparticle film. Three typical response regions with different conductance-hydrogen pressure correlations were observed. It was found that the α - β phase transition region of palladium hydride moves to significant higher hydrogen pressure with the addition of nickel element, which greatly enhance the hydrogen sensing performance of the nanoparticle film.

1 Introduction

In recent years, hydrogen has become an important new alternative energy source which can be used in various fields, including fuel cells, metallurgical, and electronic industries. However, hydrogen is flammable and explosive when its concentration exceeds 4% in air [1]. Hence, immediate detection of hydrogen becomes an important issue. Because of the broad range of fields of application, sensitive hydrogen detectors that can work over a very wide range of temperatures (including room temperature) and pressures or hydrogen gas concentrations are critically required not only for leak detection but also for monitoring and controlling flow and hydrogen purity. Although some commercial hydrogen sensors are currently available, a universal hydrogen detector that can meet the above requirement is still lacking.

A significant interest has been developed on metallic nanostructure based sensors for gases and biomolecules, with their ultrahigh detection ability. Recently, Pd nanoparticle arrays have been used to fabricate highly selective sensors for the detection of hydrogen gas [2]-[4]. It has been demonstrated that hydrogen sensing using Pd nanostructures may be able to exceed the performance of existing hydrogen sensors in both response speed and sensitivity.

Despite the superior sensitivity of Pd-based hydrogen sensors, they have several drawbacks in applications. For example, volume expansion by hydrogen absorption causes changes in the structure of Pd thin films and results in hysteresis behavior in electrical resistance [5]. In addition, the phase transition from α phase of Pd to the

“hydride” β phase occurs at fairly low hydrogen partial pressures, and this transition leads to irreversible structural changes in Pd[6, 7]. To improve these drawbacks, films of Pd-based alloys, such as Pd-Mg[8], Pd-Au[9], Pd-Ag[10], and Pd-Ni[11-13] alloys, have been investigated. Among these candidates, the Pd-Ni alloy has been spotlighted due to its durability and fast response.

In this paper, we fabricate films of Pd-Ni alloy nanoparticles by gas phase cluster beam deposition with controlled coverage. We study the modification of the α to β -phase transition and hydrogen sensing behaviors of the Pd nanoparticles with nickel additions.

2 Experimental

The deposition of Pd-Ni nanoparticles was performed in a high vacuum chamber equipped with a magnetron plasma gas aggregation cluster source [14]. The Pd-Ni nanoparticles were formed in the aggregation tube of the cluster source. The aggregation tube was cooled with liquid nitrogen and maintained an argon stream with stable pressure of 100 Pa by introducing 80 sccm of argon gas inside. A stable magnetron discharge was operated with an input power of 60 W. Atoms were sputtered from the Pd target and the Ni target, and then clusters were formed through the aggregation process in the argon gas.

We fabricated hydrogen sensors by depositing Pd-Ni nanoparticle layers with controlled coverage on pre-deposited gold interdigital electrodes. The gold interdigital electrodes, with a 100 nm thickness and 5 μ m electrode separation, were patterned onto a silicon

^a2244767015@qq.com, ^blyuan@nju.edu.cn, ^csjhanmin@nju.edu.cn, ^dfeiliu1987@gmail.com

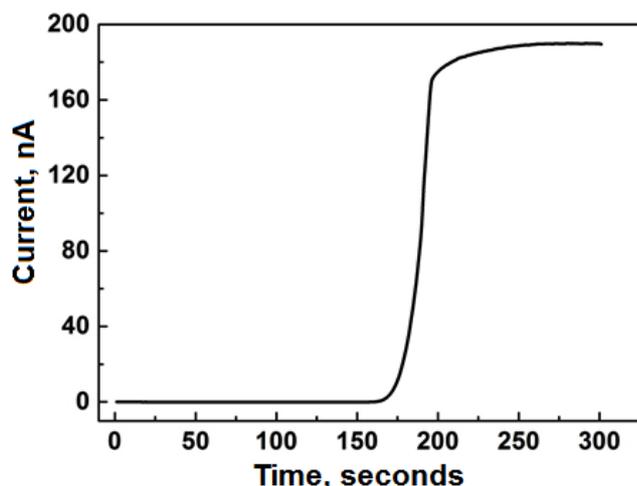


Fig. 1. Change of the electric current passing through the electrodes during Pd/Ni nanoparticle deposition. The measurement was performed with an applied bias of 1 V.

substrate with a 300 nm SiO₂ insulating surface layer utilizing a standard photolithographic lift-off process. During deposition, the current across the electrodes gap was measured in real-time with a source meter (Keithley 2400) by applying a bias of 1V. The deposition was stopped when the predetermined conductance values were attained. The characteristics of alloy with Ni contents of 0%, 17% and 60% are fabricated.

The nanoparticles were deposited on amorphous carbon films supported with copper grids for transmission electron microscope (TEM) characterization or on silicon substrate for X-ray photoelectron spectroscopy (XPS) characterization simultaneously with the sensor fabrication. The microstructures of the fabricated Pd-Ni nanoparticle films were characterized with a field-emission TEM (FEI TECNAI F20s TWIN). The composition of the nanoparticles was analyzed with XPS (ESCALABMK-II).

The hydrogen-sensing response of the fabricated sensors was studied at room temperature in a gas flow chamber. In the measurement, the sensors were exposed to alternating H₂ and vacuum cycles. Samples were loaded with hydrogen by introducing H₂ into the chamber through a mass flow controller until the predetermined pressure was attained. For deloading, the chamber was evacuated using a mechanical rotary pump. The pressure in the chamber was monitored with a piezo-resistive gauge. Simultaneously, the conductance of the sample was measured by measuring the current in the sample with the source meter for a constant bias voltage of 1 V applied to the interdigital electrodes.

3 Results and discussions

A typical characteristic of the current evolution during cluster deposition is shown in Figure 1 as a function of deposition time. The current start to increase abruptly at 168 s. Deposition is cut off by a shutter at 196 s and a sensor sample was obtained. The conductance of the device was about $1.72 \times 10^{-7} S$.

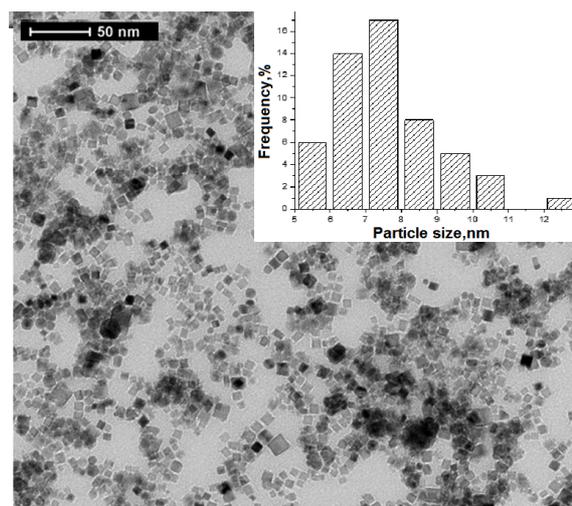


Fig. 2. A TEM micrograph of Pd-Ni alloy nanoparticle films.

A TEM micrograph of Pd-Ni alloy nanoparticle films is shown in Figure 2. As shown, the nanoparticle films are composed of randomly distributed isolated nanoparticles which form numerous closely spaced array areas. The average diameter of the nanoparticles is $7 \text{ nm} \pm 1 \text{ nm}$ which is shown at the top right corner in Figure 2. The shapes of Pd-Ni alloy nanoparticles are predominantly cuboid.

The alloying state of the Pd-Ni nanoparticles was verified with XPS. Fig. 3 shows the photoemission data of the Pd 3d core level together with Ni 2p core level measured from pure Pd or Ni nanoparticles and Pd-Ni nanoparticles with a Ni content of 17%. The binding energy of Pd 3d_{5/2} core level for the pure Pd nanoparticles was observed at about 334.9 eV, which agrees well with the metallic Pd. For Pd-Ni nanoparticles, the Pd 3d_{5/2} XPS peak shift to 335.4 eV (Fig. 3a), and the Ni 2p_{3/2} XPS peak locates at 852.0 eV (Fig. 3b), respectively. The binding energies of Ni 2p_{3/2} and Pd 3d_{5/2} in Pd₈₃Ni₁₇ alloy nanoparticles have a positive shift of about 1.4 eV and a positive shift of about 0.8 eV, respectively, as compared with those of the pure metallic Ni and Pd. Such a significant change in the electronic state of Pd atoms caused by Ni incorporation confirms the formation of an alloy phase.

Figure 4 shows the current response curve (current versus time diagram) measured for the Pd-Ni nanoparticle arrays with 17% Ni content. The curve shows that for each hydrogen loading-deload cycle the current, which corresponds to the increase of the conductance of the nanoparticle array, increases quickly once the device is exposed to hydrogen. At longer exposure time, the rate of current increase becomes lower. As hydrogen is deloaded, when the hydrogen pressure is between 0 Pa and about 3000 Pa, the conductance essentially returns to its original value. However, as the pressure becomes higher, the conductance can't return to its original value and a baseline drop is observed. We found that the baseline variance was related to the transition from the α -phase to the hydride β -phase of the Pd-Ni nanoparticles. For the Pd-Ni nanoparticle arrays

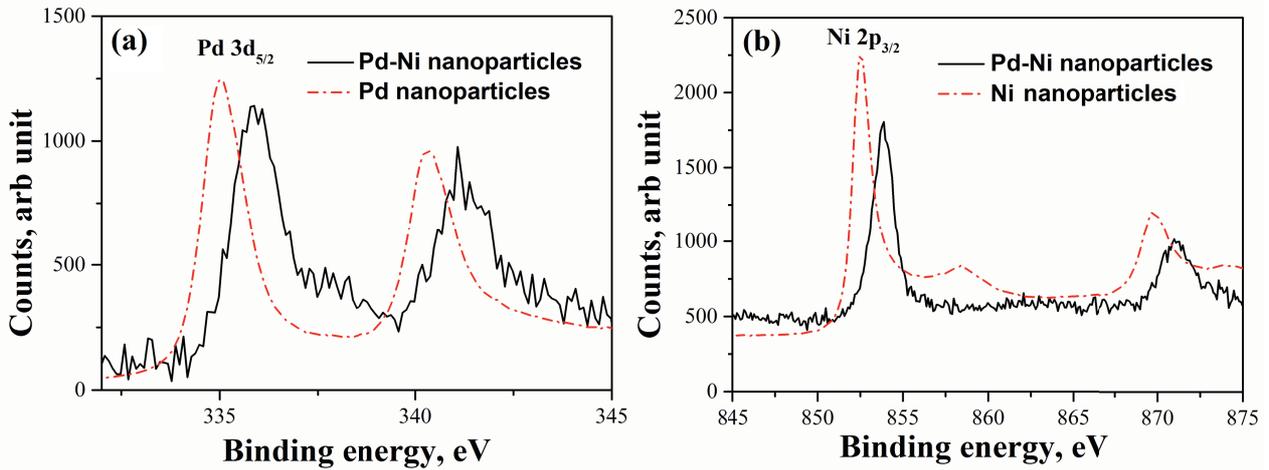


Fig. 3. (a) Pd 3d core level spectra of Pd-Ni nanoparticles; (b) Ni 2p core level spectra of Pd-Ni nanoparticles.

with 60% Ni content, no hydrogen response could be observed.

A log-log plot of the relative changes in conductance versus H_2 pressure is shown in Figure 5. In Figure 5, the relative changes in conductance was defined as $(G-G_0)/G_0$, where G_0 is the base conductance at zero hydrogen loading, and the corresponding hydrogen pressure was measured as the peak pressure of each hydrogen loading, which is indicated on the top of the peak for every single loading and deloading cycle in Figure 4.

Three typical response regions can be distinguished in Figure 5. For the pure Pd nanoparticle array, at low H_2 pressure (<1kPa), a relative low-pitched increment of the conductance with H_2 pressure is observed. Over a narrow H_2 pressure range of 1–3kPa, a dramatic increase of the conductance with H_2 pressure induces a 5–50% change in $\Delta G/G_0$. Across this H_2 pressure range, the Pd hydride undergoes a first-order phase transition from α -PdHx to β -PdHx and α and β phases co-exist [15]. The increase of the conductance is directly related to the shrink of the gaps between the nanoparticles, as a result of the expansion of the Pd nanoparticles due to hydrogen absorption. For H_2 pressure >3kPa, the Pd hydride has fully transformed to β -PdHx phase, the rate of conductance change falls abruptly. However, monotonic correlations of the conductance with H_2 pressure can still be observed.

For the Pd-Ni nanoparticles with 17% Ni content, the α - β phase transition starts from 3.5kPa and ends at about 7.0kPa, which corresponds to H_2 concentration of 3.5% and 7.0% at atmospheric pressure. The α - β phase transition occurs at a hydrogen pressure much higher than the pure Pd nanoparticles and well locates near the explosion limit of 4% hydrogen concentration at atmospheric pressure. Therefore, the sensitivity of hydrogen detection in the hydrogen pressure near explosion limit becomes much enhanced. Furthermore, the conductance change in the hydrogen pressure region below 7.0kPa becomes quite regular, which enables the possibility to quantitatively detect hydrogen in this hydrogen pressure region. It is obvious that the hydrogen sensing performance of the Pd nanoparticle films is greatly enhanced with the addition of the nickel element.

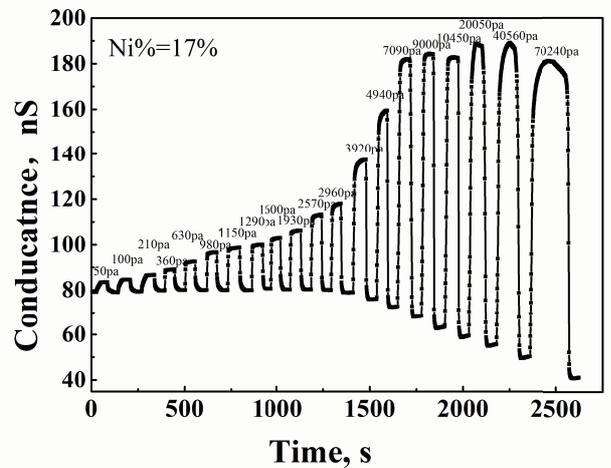


Fig. 4 Hydrogen sensing electrical conductance response curves for $Pd_{83}Ni_{17}$ nanoparticle films exposed to alternating loading/deloading cycles of H_2 gas. The pressure of each H_2 gas loading is indicated on the top of the peak.

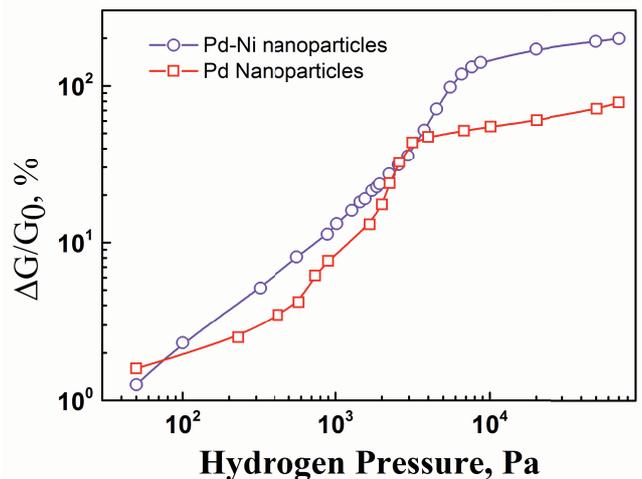


Fig. 5 Log-log representation of the relative changes in conductance ($\Delta G/G_0$) as a function of hydrogen pressure.

4 Conclusion

We demonstrate a gas phase route to prepare Pd-Ni nanoparticle films with controlled size and dispersity by

cluster beam deposition. The composition of the film is dominated with Pd-Ni nanoparticles of 7nm mean diameter. The formation of Pd-Ni nano-alloys was confirmed by X-ray photoelectron spectroscopy measurements. Hydrogen sensor based on dense Pd-Ni alloy nanoparticle arrays deposited on interdigital electrodes has been demonstrated. The sensor is a resistance-based device operates at room temperature and shows high sensitivity. It has been shown that the Ni content in the nanoparticle has an obvious effect on the hydrogen response behavior corresponding to the conductance change of the nanoparticle film. Three typical response regions with different conductance-hydrogen pressure correlations were observed. The intermediate regime, corresponds to hydrogen pressure from 3.5kPa to 7.0kPa, has a dramatic change of conductance induced by H₂ pressure change, which gives rise to a very high sensitivity and neglectable temperature influence. This region is corresponding to the α -to- β phase transition of Pd, It was found that the α - β phase transition region of palladium hydride moves to higher hydrogen pressure with the addition of nickel element, which greatly enhance the hydrogen sensing performance of the nanoparticle film.

Acknowledgements

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