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Detecting hydrogen gas by single electron tunneling based sensors: an image processing and simulation study

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Abstract. We present a hydrogen sensor based on single electron tunneling at two dimensional (2D) hexagonal closed packed arrays of palladium nano-islands. Parameters of the hexagonal closed packed arrays of palladium nanoparticles were extracted from experimental TEM results by image processing methods. Using SIMON simulator, emergences of the coulomb blockade were inspected by studying Current-Voltage (IV) characteristics of equivalent circuits consisting of palladium islands and tunneling junctions. After ensuring the emergence of Coulomb blockade phenomena in these arrays, the possibilities of using these arrays as an ultra-low power consumption hydrogen sensor were studied. The changes in IV characteristics were investigated after exposing to hydrogen gas according to the lattice parameter expansion of palladium nanoparticles at different pressures of hydrogen gas. The change in the resistance of the device before and after exposing to hydrogen was extracted. The obtained results show that this configuration shows single electron tunneling and can be used as the hydrogen gas sensor. The response of the sensor is less than 15 seconds with measuring range as low as 0.5% H_2.

Keywords: Monodisperse Palladium Nanoparticles, Hydrogen gas sensor, Single electron tunneling, Electrical resistance, Ultra-low Power Consumption

1. INTRODUCTION

Hydrogen gas because of advantages such as cleanliness, natural abundance, chemical reactivity and recyclability has attracted a great deal of attention in industrial and engineering processes [1]. Nonetheless, concentrations of hydrogen gas more than 4% in air are highly flammable [2]. For this reason fast and reliable detection of hydrogen gas is required. Numerous hydrogen gas sensors have developed and studied over the years [3]. The mentioned sensors operate based on the change in different properties of selective material upon adsorption and desorption of the hydrogen. Palladium's specific size-dependent behavior upon adsorption and desorption of hydrogen gas makes palladium nanoparticles of interest for hydrogen gas sensing [4, 5].

By developing patterns of palladium nanoparticles, their specific behavior can be put under use in order to detect hydrogen gas. In a new hydrogen sensor developed by J. Van Lith and coworkers, the cluster film had coverage below the percolation threshold, and the main conduction paths were contained tunneling gaps, which dominate the resistance. Upon exposure to hydrogen the palladium clusters expand, reducing the average size of the tunneling gaps, which decreases the resistance of the film [6]. Other possible patterns for developing hydrogen sensors with tunneling gaps are arrays of palladium nanoparticles with controlled size and width of the gaps between them. Sang-Wook Kim and coworkers have synthesized monodisperse palladium nanoparticles with particle sizes of 3.5, 5, and 7 nm from the thermal decomposition of a palladium-surfactant complex. Their results show that, perfectly ordered arrays of close to identical nanoparticles (NPs) with hexagonal closed packed structure can be synthesized [7]. It must be noted that unlike other methods for synthesizing palladium nanoparticles, using this

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method palladium nanoparticles does not connect to each other even after exposure to hydrogen gas and only the size and width of the gaps between nanoparticles change. An important fact about 2D hexagonal closed packed arrays is that, ultra large arrays of palladium nanoparticles can be synthesized. Jongnam Park and coworkers have succeeded to synthesize ultra large arrays of palladium nanoparticles up to 40 gr of metal nanoparticles [8].

If the widths of the gaps between adjacent palladium nanoparticles be small, each less than 10 nm, then an applied voltage difference across the electrodes can transfer electrons on to, and off the islands by quantum mechanical tunneling [9]. The gaps subsequently form tunnel barriers with an associated energy. In such a systems single electron tunneling occurs. Synthesized palladium nanoparticles will create a multiple-island single electron chains with tunneling barriers. The essential parameters in single electron devices are capacitance and resistance of tunneling junctions. The multiple-island single-electron chains of tunneling junctions are promising for the development of a variety of devices due to their ultra-low power consumption, and high-sensitivity [10-12]. Their main advantages in comparison with respect to single-island single-electron transistors (SETs) with identical dimensions of islands and tunneling junctions are a higher threshold voltage of Coulomb blockade, less sensitivity to unwanted effects such as defects and background charges, less sensitivity to uncertainty of the diameter of palladium nanoparticles, higher operation temperature and ease of fabrication.

In this paper, we demonstrate a hydrogen sensor by single electron tunneling at 2D hexagonal closed packed arrays of palladium nano-islands arranged between two electrodes. First, we obtain size distribution and spacing of these arrays using image processing methods from monodisperse palladium nanoparticles synthesized by Sang-Wook Kim and coworkers [7]. Then we investigate the IV characteristics of the equivalent circuits at room temperature. From the obtained results, we investigate the emergence of Coulomb blockade and occurring single electron tunneling. The main goal in this paper is showing the applicability of 2D arrays as single electron devices. In order to show this we design and simulate a hydrogen sensor from 2D arrays of palladium nanoparticles. We use experimental data extracted from reference [13] in order to calculate palladium nanoparticles size expansion according to lattice parameter variation. We calculate the sensitivity, power consumption and measuring range of this sensor according to the model proposed by J. Van Lith and coworkers [6].

2. ASSUMPTIONS OF THE MODEL

2D hexagonal closed packed arrays of palladium nanoparticles between two electrodes were assumed. Required parameters for simulations involving size distribution of palladium nanoparticles and junction width between them were obtained from TEM results of the 2D hexagonal closed packed arrays synthesized by Sang-Wook Kim and coworkers, which are shown in figure 1[7, 13]. The obtained parameters and also other parameters used in the simulations are shown in table 1. The diameter of nanoparticles shows Gaussian distribution with narrow full width at half maximum (FWHM).

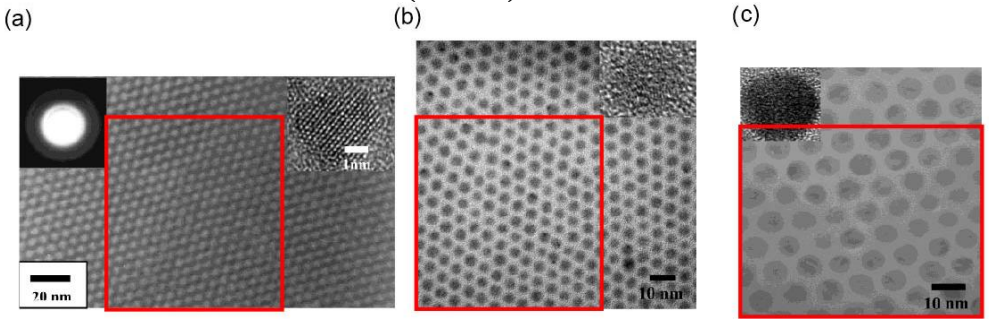

Figure 1. TEM images of arrays of a) 3.5 nm, b) 5 nm and c) 7 nm palladium nanoparticles synthesized by Sang-Wook Kim and coworkers.

As mentioned before, two essential parameters in single electron devices are tunneling resistance and tunneling capacitance. We assume that the tunneling resistance between nanoparticles can be described by [14]:

$$R \propto e^{\beta L} e^{E_C/kT} \quad (1)$$

Where L is the size of the tunneling gap. Here, the activation energy E_C is the Coulomb charging energy and β is a system dependent tunneling constant given by $\beta = \sqrt{8mU_0/\hbar^2}$ [14], with m as effective mass of an electron. For avoiding several simultaneous tunneling, minimum tunnel resistance of all the tunnel barriers must be much higher than quantum unit of resistance R_Q ($R \gg R_Q = \frac{h}{e^2} \sim 26.5\ \mathrm{K\Omega}$) where e is the elementary charge of electron and h is Plank constant [15, 16]. Tunneling capacitance also can be calculated by:

$$C_{12} = \frac{4\pi\epsilon ab}{d} \sin(\mathrm{h}\,U) \sum_{n=1}^{\infty} [\sinh(nU)]^{-1} \quad (2)$$

Where a and b are the radii of palladium nanoparticles and dimensionless parameter U is related to a, b and c by $\cosh(U) = \frac{c^2 - a^2 - b^2}{2ab}$. Here, c is the center-center distance between adjacent palladium nanoparticles.

Table 1. Extracted parameters from experimental results that are used in simulations.

Mean Diameter of nanoparticles	3.5 nm	5 nm	7 nm
Full Width at Half Maximum	0.11 nm	0.52 nm	0.59 nm
Lattice parameter before exposing to hydrogen gas	$3.908\mathring{A}$	$3.90\mathring{A}$	$3.90\mathring{A}$
Lattice parameter after exposing to hydrogen gas	$3.96\mathring{A}$	$3.97\mathring{A}$	$3.98\mathring{A}$

The results obtained for lattice parameter of the palladium nanoparticles by Bridget Ingham and coworkers via In situ synchrotron X-Ray diffraction experiments on bare palladium nanoclusters with size selected (1.7, 3 and 6.0 nm) were used [13]. According to their results, palladium nanoparticles form hydride phases and a change (Δα) occurs in the lattice parameter (α) due to the change in the external hydrogen pressure. The variation (Δα) in lattice parameter cause the change (Δd) in diameter (d) of palladium nanoparticles (Δd= (Δα/α) d). Therefore, according to relations (1) and (2) the tunneling resistance and tunneling capacitance between adjacent nanoparticles change. The change in tunneling resistance in its turn changes the total resistance of the array and the electric current that passes through the array. The change in the total resistance of the array will be used as the sensing parameter of hydrogen gas. The change in lattice parameter of 6 nm palladium nanoparticles were used for 5 and 7 nm palladium nanoparticles. The lattice parameters used for palladium nanoparticles before and after exposing to hydrogen gas is shown in table 1.

An important factor in the hydrogen gas sensors is their response with respect to hydrogen pressure. For measuring response of palladium nanoparticles to hydrogen gas, the model proposed by J. Van Lith and coworkers was employed. According to their proposed model: (1) a variation in external hydrogen pressure consequences in a variation (Δα) in the lattice constant (α), (2) a variation in lattice constant changes the nanoparticles diameter (d), (3) a variation in cluster size changes the mean tunneling gap, and (4) a variation in the mean tunneling gap changes the resistance R.

3. SIMULATION METHOD

We selected sections of figure 1 and obtained equivalent circuits, which are shown in figure 2. Using SIMON2.0, we investigated IV characteristics of equivalent circuits. The SIMON2.0 is a single electron device and circuit simulator which employs Orthodox theory and Monte-Carlo methods to simulate the propagation of electrons in a wide variety of single electron circuits [17]. Orthodox theory is a semi-classical approach, which assumes that (i) the energy spectrum of the conductive islands may be considered continuous (ii) the tunneling time is negligible compared to the time between tunneling events, and (iii) coherent tunneling events are ignored [9].

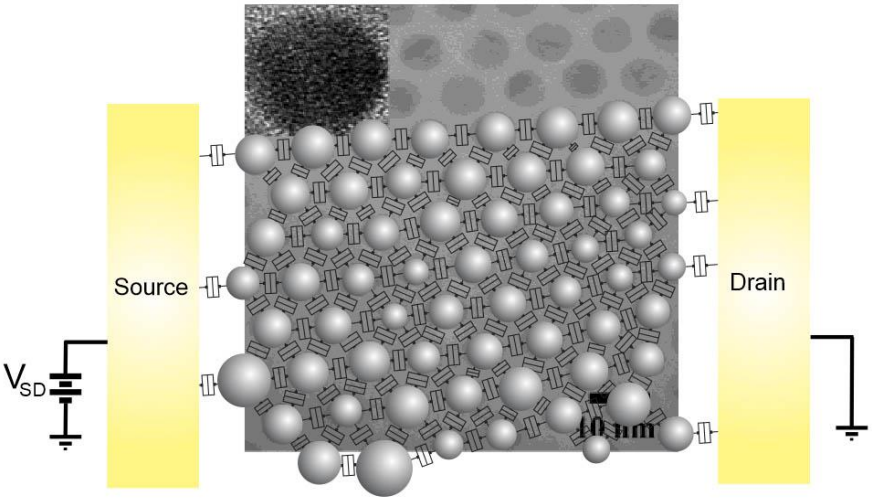

Figure 2. Schematic diagram of equivalent circuits consisting palladium nano-islands and tunneling junctions.

After setting some parameters like temperature, mode of simulation, capacitances and resistances of tunneling junctions, we plotted IV characteristics. The values of tunneling resistances and capacitances calculated from equations (1) and (2) was used for simulations. The calculated tunneling resistance values were greater than the quantum unit of resistance. Furthermore, the temperature of 300 K (the temperature for detecting hydrogen) were used in simulations.

4. DISCUSSION AND RESULTS

Figure 3 shows the IV characteristics for selected section of arrays of palladium nanoparticles in figure 1, which are plotted at room temperature (300 K). In the inset of figure 3 the Gaussian distribution obtained from image processing of 2D hexagonal packed arrays are shown. As it can be seen from figure 3, Coulomb blockade emerges in these arrays which confirm the occurrence of single electron phenomena. With increasing the diameter of nano-islands, coulomb blockade threshold decreases. The reason for this is that, coulomb blockade threshold is related to the capacitance of tunneling junction and with increasing diameter of nanoparticles and junction width between them coulomb blockade threshold changes.

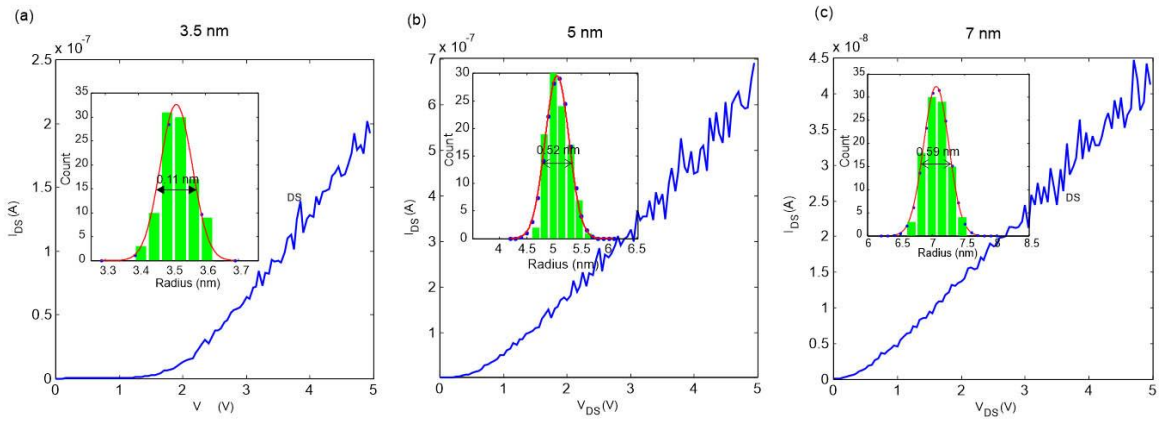

Figure 3. IV characteristics of selected sections of arrays for a) 3.5 nm, b) 5 nm and c) 7 nm nano-islands.

The possibilities of using these arrays as single electron devices were put into investigation by designing and simulating a hydrogen sensor. To reach this goal the changes in IV characteristics of the arrays were studied upon exposure to hydrogen gas. For simulations involving hydrogen gas, the change in tunneling resistance and capacitance were calculated for each tunneling junction - from equations (1) and (2) - according to lattice parameter expansion at different pressures. By exposing the arrays into hydrogen gas, the IV characteristics change considerably and are separated completely before and after exposing to hydrogen. The reason for this is that upon exposure to hydrogen, diameter of nano-islands expands and junction widths decrease and consequently, total resistance of the arrays declines and current passing through the array rises. It must be noted that the IV characteristics shown in figure 4 are plotted at selected hydrogen pressure of 20 torr. By increasing partial pressure of hydrogen gas, the separation between IV results before and after exposing to hydrogen increases. For further investigation and becoming sure about functionality of these arrays, we assumed similar arrays with Gaussian distributions. Diameter of every nano-island changed in each simulation according to Gaussian distribution, and IV characteristics were plotted. In figure 5 some of the results before and after exposing to hydrogen is shown in which IV characteristics that exhibit maximum and minimum resistances are involved. With the results obtained up to now, we can say that 2D hexagonal closed packed arrays can be used as single electron devices in nano-electronics.

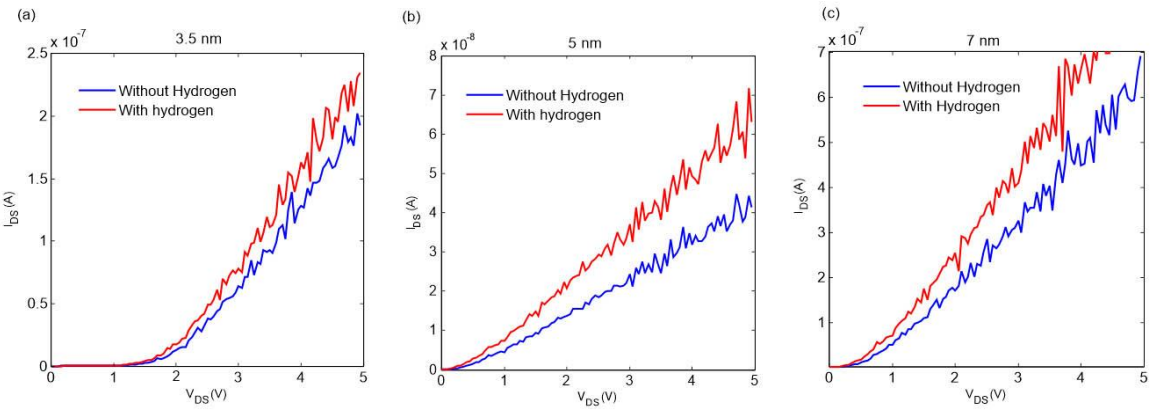

Figure 4. Effect of hydrogen gas on the IV characteristics of selected sections of arrays for a) 3.5 nm, b) 5 nm and c) 7 nm nano-islands.

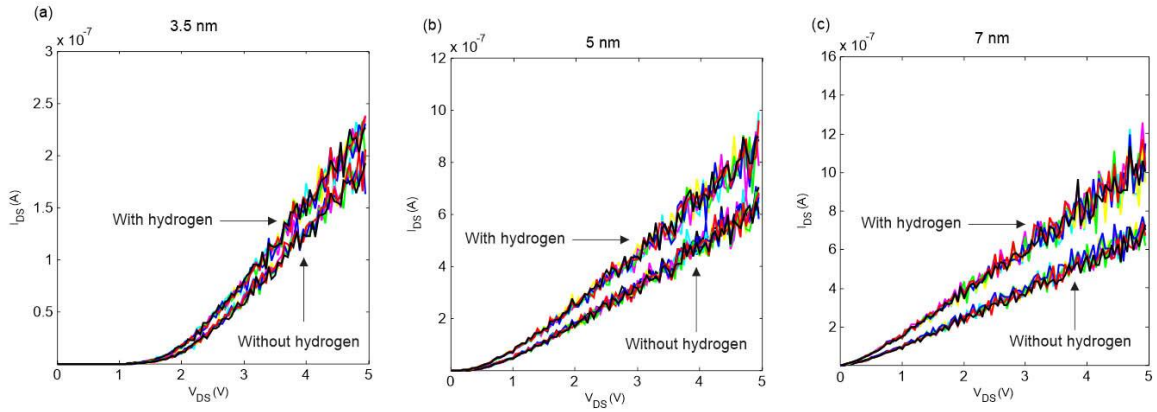

Figure 5. Investigation of functionality of these arrays as 2D single electron devices.

An important factor in hydrogen sensors is their response. Taking into account the four steps, J. Van Lith and coworkers measured a response time about 15 s for different concentrations of hydrogen gas. Their developed sensor can detect hydrogen concentration as low as 0.5% hydrogen gas. Though the configuration assumed in our paper is somehow different from J. Van Lith and coworkers, but it's actually the four steps that determine the response of the sensor. According to the four steps mentioned, and due to similarities of size of the palladium nanoparticles assumed in our paper, we expect that the response time and measuring range be similar to theirs.

Electrical currents obtained in the results are less than 10 nA. Therefore, by selecting suitable working voltage of the sensor at voltages slightly more than the coulomb blockade threshold we can have a sensor with power consumption of 1 nw. This ultra-low power consumption is another strength point and advantage of this hydrogen sensor compared to other sensors.

5. CONCLUSIONS

Conventional single electron devices are subject to several disadvantages, which make their operation distrustful and also their control difficult. Two-dimensional arrays of nanoparticles were proposed as an alternative to conventional SE single island devices. We considered arrays of monodisperse palladium nanoparticles between two electrodes by configuration obtained using image processing method. The emergence of Coulomb blockade in 2D hexagonal closed packed array of palladium nanoparticles and possibility of these arrays as single electron devices were investigated. IV results obtained from equivalent circuits show that Coulomb blockade emerges in these arrays. A hydrogen sensor designed from these arrays ensures the possibility of using these arrays as an alternative to conventional single electron devices. Applying four steps provided by J. Van Lith et al, this sensor can detect hydrogen gas as low as 0.5% with a response time of less than 15 seconds. According to IV characteristics, this sensor with power consumption of less than 1 nW is an ultra-low power sensor.

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