Single-Electron Tunneling Based Hydrogen Sensor

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We present a hydrogen sensor based on single-electron tunneling in two dimensional (2D) hexagonal closed packed arrays of palladium nano-islands. The parameters of the palladium nanoparticles were extracted from the experimental TEM results by the image processing method. We also assumed random offset charges for every palladium nanoparticle. Using the SIMON simulator, the emergence of Coulomb blockade was inspected by studying the current-voltage (IV) characteristics of equivalent circuits consisting of palladium islands and tunneling junctions. After ensuring the emergence of the Coulomb blockade phenomena in these arrays, the possibilities for using these arrays as a hydrogen sensor were studied. The change in the tunneling resistances and capacitances were calculated according to the lattice parameter expansion of the palladium nanoparticles at different pressures of the hydrogen gas. The changes in the IV characteristics were investigated after exposing the arrays into hydrogen gas. The change in the resistance of the arrays before and after the exposure to hydrogen were extracted. According to the results, this configuration shows single-electron tunneling and can be used as a hydrogen gas sensor.

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I. INTRODUCTION

Hydrogen gas, due to 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 been developed and studied over the years [3]. The mentioned sensors operate based on the change in different properties of a 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 into use in order to detect hydrogen gas. There are patterns in which palladium nanoparticles are synthesized with a controlled size and width of the gaps between them. 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 (Fig. 1). Their results show that perfectly ordered arrays of close to identical nanoparticles (NPs)
with hexagonal closed packed structure can be synthesized [6]. It must be noted that in this method the palladium nanoparticles do not connect to each other even after exposure to hydrogen gas, and only the size and width of the gaps between the nanoparticles change. An important fact about 2D hexagonal close packed arrays is that ultra large arrays of palladium nanoparticles can be synthesized. Park and coworkers have succeeded in synthesizing ultra large arrays of palladium nanoparticles up to 40 gr of metal nanoparticles [7].

FIG. 1: TEM images of 2D hexagonal closed packed arrays synthesized by Kim et al. [6].

If the widths of the gaps between the adjacent palladium nanoparticles is small, each less than 10 nm, then an applied voltage difference across the electrodes can transfer electrons on to, and off from the islands by quantum mechanical tunneling [8]. The gaps then form tunnel barriers with an associated energy. In such a system single-electron tunneling occurs. Deposited palladium nanoparticles will create multiple-island single-electron chains with tunneling barriers. 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 [9–11]. Their main advantages are a higher threshold voltage of Coulomb blockade, less sensitivity to background charges, higher operation temperature, and ease of fabrication.

In this paper, we demonstrate a hydrogen sensor by single-electron tunneling in 2D hexagonal closed packed arrays of palladium nano-islands arranged between source-drain electrodes. First, we obtain size and tunneling gap distributions of these arrays using an image processing method from monodisperse palladium nanoparticles synthesized by Kim et al. [6]. We also assume random offset charges between $-e$ and $e$ for the palladium nanoparticles [12]. 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 the occurrence of single-electron tunneling. We use experimental data extracted from reference [13] in order to calculate the palladium nanoparticles size expansion according to the lattice parameter variation. Finally, we calculate the properties of this sensor.
II. ASSUMPTIONS OF THE MODEL

We obtained the size and tunneling gap distribution arrays shown in Fig. 1 by the image processing method. Gaussian distributions were obtained for them. Fitting of the obtained data confirmed the Gaussian distributions. The parameters of size and tunneling gap distribution, including the mean size and full width at mid height (FWHM) are shown in Table I.

<table>
<thead>
<tr>
<th>Size of nanoparticles</th>
<th>3.5 nm</th>
<th>5 nm</th>
<th>7 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean diameter of nanoparticles</td>
<td>3.5 nm</td>
<td>5 nm</td>
<td>7 nm</td>
</tr>
<tr>
<td>FWHM of diameter distribution</td>
<td>0.11 nm</td>
<td>0.52 nm</td>
<td>0.59 nm</td>
</tr>
<tr>
<td>Lattice constant before exposing to hydrogen</td>
<td>3.908 Å</td>
<td>3.9 Å</td>
<td>3.9 Å</td>
</tr>
<tr>
<td>Lattice constant after exposing to hydrogen</td>
<td>3.96 Å</td>
<td>3.98 Å</td>
<td>3.98 Å</td>
</tr>
<tr>
<td>Mean tunneling gap</td>
<td>1.9 nm</td>
<td>2.2 nm</td>
<td>2.5 nm</td>
</tr>
<tr>
<td>FWHM of tunneling gap distribution</td>
<td>0.15 nm</td>
<td>0.6 nm</td>
<td>0.7 nm</td>
</tr>
</tbody>
</table>

A general problem in the implementation of all SET-based devices is the high sensitivity of the constituent SETs to random offset charges. Clearly, very good control over offset charge is necessary to develop a practical SET based device. This charge consists of the charge induced on the island due to the trapped charges in the SET, near the island. As the offset charge is simply an induced charge, created by a shift in the electron distribution on the island, relative to the fixed ionic cores, it is not quantized and may have a value which is a fraction of $e$. Therefore, in our simulations we consider a random offset charge between $-e$ and $e$ for every island [12].

The essential parameters in multiple-island single-electron chains are the resistance and capacitance of the tunneling junctions. We assume that the resistance of the tunneling junctions can be described by [14]:

$$ R_{ij} = \left( \frac{h^3}{64\pi^2 m_e e^2} \right) \left( \frac{E_f + \phi_{\text{eff}}}{E_f} \right)^2 \frac{\exp(2\beta k_0 d_{ij})}{\phi_{\text{eff}}} \left( \frac{\beta k_0}{r_a} \right) \frac{1}{G_{ij}}, $$

where $\phi_{\text{eff}} = \phi - e V_{ij}/2$, $V_{ij}$ is the potential drop across the two islands and $\phi$ is the work function of palladium nanoparticles, $k_0 = (2\pi/h)(2m_e \phi_{\text{eff}})^{1/2}$, $h$ is the Planck constant, and $m_e$ is the free electron mass. $\beta$ is an enhancement parameter that was taken to be 0.115. Approximate values of $E_f$ and $\phi$ for palladium nanoparticles have been chosen as 5.75 eV and 5.12 eV, respectively. The average radius of the two spherical islands forming the junction is $r_a$, and $d_{ij}$ is the closest distance between their surfaces (the junction width). $G_{ij}$ is a purely geometrical factor $G_{ij} = 1 - \left( \frac{r_a}{r_a + d_{ij}} \right)^2$.
An analytical method employing image charges was used for the calculation of junction capacitances $C_{ij}$ between neighboring islands \([15, 16]\):

$$C_{ij} = \frac{4\pi \varepsilon_0 r_i r_j}{c} \sinh(U) \sum_{n=1}^{\infty} \left[ \sinh(nU) \right]^{-1},$$

(2)

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

An explanation to the effect of discontinuous palladium can be given in terms of both the work function variations and island expansions. The observation of a fast rise in resistance is due to a work function increase, the accompanying slower resistance decrease to the islands increasing in size is owing to the lattice expansion given by bulk adsorption \([17]\). At room temperature, palladium forms hydride phases due to hydrogen absorption. Therefore, the lattice parameter of palladium nanoparticles shows a hysteresis loop during adsorption and desorption of hydrogen. Ingham and coworkers have investigated the behavior of bare palladium upon hydrogen gas, and they obtained the variation of the lattice parameter versus hydrogen pressure \([13]\). We use the results obtained by them for the lattice parameter of selected sizes of 3 and 6 nm in our studies. The expansion of individual nanoparticles increases the area occupied by each nanoparticle, and this in turn decreases the average size of the tunneling gap. Thus, according to Equations (1) and (2) the resistance and capacitance of the tunneling junctions change.

Owing to the expansion of the palladium nano-islands, we employ the following steps in order to calculate the new resistance and capacitance of the tunneling junctions. (1) a change ($\Delta a$) occurs in the lattice parameter ($a$) due to the change in the external hydrogen pressure. (2) The variation ($\Delta a$) in the lattice parameter causes the change ($\Delta d$) in the diameter ($d$) of the palladium nanoparticles ($\Delta d = (\Delta a/a)d$). (3) The expansion of individual nanoparticles increases the area occupied by each nanoparticle, and this in turn decreases the average size of the tunneling gap ($L$). In general, the change in $L$ is given by $\Delta L = -pdL\Delta a$. (4) Therefore, according to relations (1) and (2) the resistance and capacitance of the tunneling junctions change. Furthermore, a temperature of 300 K (the temperature for detecting hydrogen) was used in the simulations. In reality, hydrogen will change slightly the band in palladium nanoparticles, and accordingly will change beta in expression (1) as well. We found this effect to be not important in comparison with the tunneling gap ($L$) on the IV characteristics, and in the following we only consider the change in the tunneling gap ($L$). This is in agreement with the results obtained by Fan Wu et al. \([17]\). According to their results at room temperature by increasing the hydrogen partial pressure more hydrogen atoms are adsorbed into the metal island, and the effect of the island expansion becomes comparable with or greater than the effect of the work function increase. This is one of the reasons we choose the partial pressure of 20 torr in our investigations.
III. SIMULATION METHOD

We assumed $11 \times 11$ arrays of palladium nanoparticles based on the arrays shown in Fig. 1. The arrays were biased by a source-drain voltage $V_{ds}$ which was set from 0 to 5V. Equivalent circuits are shown in Fig. 2. Using SIMON 2.0, we investigated the IV characteristics of the equivalent circuits. The SIMON 2.0 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 [18]. 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 [8].

![Fig. 2: Equivalent circuit of 2D hexagonal closed packed array of palladium nanoparticles.](image)

After setting some parameters like the temperature (300 K), mode of simulation, random offset charges, and capacitances and resistances of the tunneling junctions, we plotted the IV characteristics.
IV. RESULTS AND DISCUSSION

Fig. 3 shows the IV characteristics for the $11 \times 11$ arrays of palladium nano-islands, which are plotted at room temperature (300 K). In the inset to Fig. 3, the size distribution of the palladium nanoparticles used in the simulations are provided. Also shown in this figure are the linear extrapolations to zero electrical current, which represent the basic conceptual principle of threshold voltages [19]. In the simulation of the IV characteristics in Fig. 3, random offset charges between $-e$ and $e$ for every nano-island are assumed. As can be seen from Fig. 3, Coulomb blockade is clearly observed in these arrays. Linear extrapolations resulted in 1.47, 0.85, and 0.53 V values for the Coulomb blockade threshold voltage ($V_{th}$) of the 3.5, 5, and 7 nm arrays, respectively, without hydrogen. With increasing the diameter of the nano-islands, the Coulomb blockade threshold decreases. We remark that the possible reason for this is that the Coulomb blockade threshold is inversely related to the total capacitance of the array [8], and with increasing diameter of the nanoparticles the total capacitance decreases.

The possibilities of using these arrays as single-electron tunneling based hydrogen sensors were put into investigation. To reach this goal the changes in the IV characteristics of the arrays were inspected upon exposure to hydrogen gas. For these arrays to become applicable as a hydrogen sensor at room temperature they must detect concentrations less than 4% in air. Using the relation $\frac{P}{760 \text{torr}} \times 100$, it turns out that the partial pressures of hydrogen gas must be less 30 torr in order for the concentration of hydrogen gas in air to be less than 4%, in this relation $P$ is the partial pressure of hydrogen gas and 760 torr is the pressure of the atmosphere. According to this simple calculation, we choose the partial pressure of 20 torr for our calculations. We need a partial pressure in our calculations since the variation of the lattice parameter is given versus the partial pressure of hydrogen gas, and also for 20 torr the lattice parameter is known. The change in tunneling
resistance and capacitance were calculated for each tunneling junction according to the procedure mentioned in the assumptions of the model. Then the IV characteristics with the assumed random offset charges, size distributions, and new parameters were plotted. The IV characteristics of the arrays after exposing to hydrogen are shown in Fig. 3. By exposing the arrays into hydrogen gas, the IV characteristics separate before and after exposing to hydrogen. The reason for this is that upon exposure to hydrogen, the diameter of the nano-islands expands and the junction widths decrease and, consequently, the total resistance of the arrays declines, and the current passing through the array rises. Also linear extrapolations show that the Coulomb blockade threshold is decreased. The new values of $V_{th}$ are shown in Fig. 3.

We also carried out Monte-Carlo simulations in which we changed the diameter of every nano-island — according to the Gaussian distribution — and their offset charges randomly in each simulation. In Fig. 4 some of the results are shown, in which the IV characteristics that exhibit the maximum and minimum changes are involved. As can be seen from Fig. 4, the IV characteristics overlap, which shows that the IV characteristic is not sensitive to the random offset charge and size distribution of the nano-islands. Multi-junction arrays provide some sort of averaging effect which makes them immune to random offset charges. Our results for random offset charges are in agreement with the results obtained by Wasshuber [12]. The results of the Monte-Carlo simulations confirms that the IV characteristics and current restriction region of these arrays is not dependent on the size randomization of the nanoparticles, and the response of the sensor is reliable.

![IV characteristics](image-url)

FIG. 4: Monte-Carlo study on the size and offset charge randomization of (a) 3.5 nm, (b) 5 nm, and (c) 7 nm palladium nano-islands, respectively, before and after exposing to hydrogen gas.

In Fig. 5, the IV characteristics for arrays of 3.5 nm nano-islands upon hydrogen gas with partial pressures of 0, 10, and 20 torr are shown. By increasing the hydrogen partial pressure, $V_{th}$ declines. The decrease in the $V_{th}$ will stop finally, since the lattice parameter expansion shows hysteresis behavior versus the hydrogen partial pressure. Although we did not study the effect of environment temperature variations in this work, but according to
the literature these arrays are tolerant against environment temperate variations.

An important factor in hydrogen sensors is their response. Typically metal hydrogen sensors measure resistance changes under a fixed applied voltage [3]. Detection is based on a change in electrical resistivity following absorption of hydrogen from the ambient due to the higher electrical resistance of palladium hydride compared to palladium. In our proposed sensor, the resistance at voltages greater than the current restriction region can be used in order to detect hydrogen gas. Using the relation \( P = \frac{P_{\text{flam}}}{\text{torr}} \times 100 \), it turns out that at the selected partial pressure of 20 torr for hydrogen gas our proposed sensor can detect 2.6% hydrogen gas in air, which is less than flammability concentration of hydrogen gas in air. We selected 20 torr in order to just show that this sensor can detect concentrations of hydrogen less than the flammability limit. Therefore we believe that with selecting an appropriate size of the Palladium nano-islands and distance between them, the detection of lower concentrations of hydrogen is possible. On the other hand, since this sensor is based on the single-electron tunneling between palladium nano-islands, this sensor is an ultra-low power consumption sensor.

FIG. 5: IV characteristics at various partial pressures of hydrogen gas.
V. CONCLUSIONS

We considered arrays of monodisperse palladium nanoparticles between source-drain electrodes by parameters obtained using the image processing of real 2D hexagonal closed packed arrays. We considered random offset charges between $-e$ and $e$ for nano-islands. The emergence of Coulomb blockade in these arrays and possibility of them serving as a hydrogen gas sensor were investigated. The IV results obtained from equivalent circuits show that Coulomb blockade emerges in these arrays. The IV characteristics of these arrays before and after exposing to hydrogen separate and the obtained results imply the possibility of using them as hydrogen sensor. These arrays are resistant against random offset charges and size randomization of nanoparticles. The proposed hydrogen sensor can detect 2.6% — less than the flammability limit — hydrogen in air, and with considering the single-electron base of this sensor we have an ultra-low power sensor.

References