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(article starts on next page)

Nanoscale Schottky diodes for studying the activity of aluminum nanoparticles in reaction with water

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Abstract. Hydrogen is a promising fuel for energy storage, transportation, production and consumption. At the same time, hydrogen in its pure form is not found on Earth in large quantities and therefore it is necessary to develop a technology for its production. One of the promising technologies for hydrogen production is the reaction of aluminum nanoparticles with water. At the same time, experimental studies of the elementary mechanisms of this reaction are difficult due to the aggressive properties of a concentrated alkaline solution, which is used to activate the aluminum surface. Here we show that the kinetics of the aluminum-water reaction can be monitored in real time using a Schottky nanodiode sensor, provided that the characteristic size of the nanodiode electrodes does not exceed 10 nm. The investigated nanoparticles are applied to the sensor surface by means of nanofabrication. The charge generated in the aluminum nanoparticles as a result of the reaction creates an electrical signal that is proportional to the rate of the chemical process. This makes it possible to use this technology to study the activity even of small groups of nanoparticles, when the volume of released hydrogen is insufficient to measure the reaction rate.

1. Introduction

The creation of eco-friendly and at the same time highly efficient technologies for the production, transportation and storage of energy is one of the main tasks of modern society, which will have to be solved in the near future. Recent advances in the development of hydrogen technologies have shown that the use of hydrogen as a fuel leads to qualitatively new indicators in the operation of energy generation systems and makes it possible to get as close as possible to the set goals in terms of efficiency, mobility and environmental friendliness [1,2].

At the same time, hydrogen in its pure form is not found on Earth in large quantities, sufficient for its large-scale use as a fuel. On the contrary, huge reserves of hydrogen are in a bound state in the composition of various chemical substances (e.g., water) and therefore it is necessary to develop a technology for its production. When choosing a hydrogen production technology, preference is given to those methods that do not emit carbon dioxide as a by-product and are renewable. Various methods of hydrogen production are discussed in the literature at present: electrolysis, photocatalytic decomposition of water, conversion of biomass, and others [3-5]. Another method of generating hydrogen, often seen as a potential candidate for mobile energy sources, is the reaction of aluminum and water (for example, $Al + 3H_2O \rightarrow Al(OH)_3 + 3/2H_2$) [6-8]. In pure water, the rate of the Al-water reaction is rather low, since the aluminum surface is covered with a barrier layer, which is a thin aluminum oxide film that prevents the interaction of H_2O molecules with the metal surface [9]. Thus, the Al-water reaction occurs only in the presence of extremely corrosive substances such as NaOH and KOH, which dissolve the oxide film and activate the Al surface to interact with water molecules, see figure 1a. Studies show that the chemical reactivity of Al changes dramatically when going from microscopic particles to nanoparticles and clusters. The activity of such particles can vary greatly depending on their size and shape. In addition, depending on the size of the nanoparticles, their physical properties (optical, magnetic, electrical and others) can also differ significantly [10]. At the same time, the direct study of elementary chemical processes on the surface of such particles is difficult because of the aggressiveness of the reaction medium in which they are located. As shown earlier, this problem can be solved by using sensors based on Schottky nanodiodes. When aluminium particles is deposited onto the surface of such sensors, it is possible to monitor their activity due to the processes of charge transfer between the nanoparticles and the sensor, which carry information on the kinetics of a chemical reaction in real time. It is important to note that the characteristic Schottky contact thickness in the sensor must be about 10 nm to allow charge carriers to cross the film in ballistic mode [11,12].

In this work, we use a nanodiode sensor to monitor the activity of nanofabricated aluminum nanoparticles with a diameter of 80 nm. It is shown that the nature of the interaction of such particles with water as a whole repeats the trend observed earlier for aluminium thin films [11]. However, on Al nanoparticles charge transfer is faster, which indicates a more rapid nature of the reaction on the nanoparticles.

2. Experimental

The manufacturing technology of a sensor based on a Schottky nanodiode is similar to that described elsewhere [11]. In short, the nanodiode sensor was fabricated by vacuum deposition of metal contacts onto an *n*-type Si (100) substrate (ρ = 1–10 Ohm·cm). Prior to the deposition of contacts, the Si substrate was etched in a buffer oxide solution consisting of NH_4F and HF in water for 60 s at room temperature. Then, an Au film (Schottky contact) with a thickness of 10 nm was deposited onto a polished surface of the Si substrate using electron beam evaporation at a base pressure of 5×10^{-6} Torr and an average deposition rate of 1.2 Å/s. The total Schottky contact area was 25 mm^2. To create an Ohmic contact, a Ti film with a thickness of 30 nm was deposited, followed by 50 nm Au, so that an ohmic contact with a size of 5×5 mm^2 was formed in the immediate vicinity of the Schottky contact.

The properties of the Schottky barrier in the nanodiode sensor were obtained from the analysis of current-voltage curves in the same way as described elsewhere [12]. The Schottky barrier height was φ = 0.76 eV (at ideality factor η = 1.1 and series resistance R = 80 Ohm) was measured.

A two-dimensional array of Al nanoparticles with an average particle diameter of 80 nm was fabricated on the surface of a nanodiode sensor by means of hole-mask colloidal lithography, which is described in great detail elsewhere [13]. Schematics of the sensor consisting of an array of Al nanoparticles deposited onto the surface of a planar Au/*n*-Si Schottky nanodiode is shown in Figure 1b.

A concentrated 1M NaOH solution was used in the experiments. To initiate the reaction, a drop of solution was placed on the surface of the sensor.

3. Results and discussion

The time variation of the electric signal recorded in the nandiode sensor due to charge transfer from Al nanoparticles during the Al-water reaction is shown in figure 1c. At the moment when the first contact of the sensor surface with NaOH solution occurs, the current is zero. This is most likely associated with the activation process when the natural oxide film on the surface of Al nanoparticles dissolves as a result of interaction with NaOH, opening the Al metal surface for reaction with water.

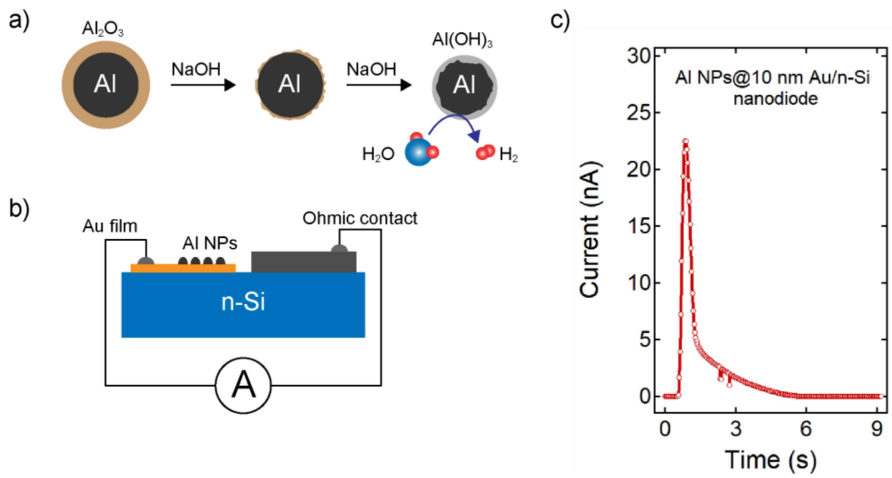

Figure 1. a) Stages of the reaction of aluminum nanoparticles with water in a concentrated NaOH solution. b) Schematic of a planar Au/n-Si nanodiode sensor with Al nanoparticles (Al NPs) deposited on its surface. c) Typical signal detected by the sensor during the Al-water reaction in 1M NaOH solution.

Approximately 0.5 seconds after contact of the NaOH solution with the surface, an electric signal caused by the Al-water reaction is detected by the sensor. As shown earlier in experiments with Al nanofilms [11], this signal reflects the chemical process on the aluminum surface. In fact, the rate of charge generation, leading to the appearance of this signal is proportional to the rate of cathodic reaction on the surface of Al nanoparticles during which hydrogen gas is released [11]. As Al particles react with water, metallic aluminum is transformed into $Al(OH)_3$ following equation 1. In this case, the electrical signal recorded by the sensor decreases, completely disappearing when the nanoparticles are completely dissolved in the NaOH solution. On the whole, this trend is similar to that observed earlier in experiments with Al nanofilms. However, the rate of the process in the case of using Al nanoparticles is higher, which is associated with their higher activity.

$$Al + 3H_2O \rightarrow Al(OH)_3 + \frac{3}{2}H_2 \quad (1)$$

Thus, by placing aluminum nanoparticles on the surface of Schottky nanodiode sensors, one can visualize elementary chemical reactions on nanoparticles and study their kinetics. This becomes possible due to two phenomena: 1) the generation of excess chemical energy due to the exothermic nature of the reaction of aluminum with water and the transfer of this energy to the electrons of the metal, and 2) the ability of mobile electrons that have received additional energy to travel significant distances exceeding the size of aluminum nanoparticles. Getting from nanoparticles into the top electrode of the Schottky nanodiode sensor, such electrons can move in a ballistic mode and reach the metal-semiconductor interface. Here, in the presence of sufficient energy exceeding the height of the Schottky barrier, electrons can overcome the barrier due to thermo-electron emission or, in the absence of sufficient energy, recharge the defects on the interface. In both cases, an electric current will be created in the nanodiode, which makes it possible to judge the number of electrons generated by the chemical reaction, as well as their energy distribution. Since the stoichiometry of the reaction of aluminum with water is known, this information makes it possible to observe the kinetics of the reaction of nanoparticles in real time.

4. Conclusion
We have shown the possibility of using sensors based on Schottky nanodiodes to study effects of charge transfer on the surface of Al nanoparticles in concentrated NaOH solutions. The electrical charges generated in Al nanoparticles during the cathodic reaction lead to an electrical signal in the sensor. This

signal transmits information on the rate of chemical processes on the surface of nanoparticles in real time, which makes it convenient to use this method for model studies of the chemical reactivity of Al nanoparticles under reaction conditions. The studies carried out in this article refer only to aluminum nanoparticles. However, it is important to note that the considered method of using Schottky nanodiodes can be used for nanoparticles made of other metals as well as for other chemical reactions. An important feature of these reactions is their high exothermicity, which can provide the electrons of the metal with sufficient kinetic energy to travel from the nanoparticle to the sensor for further detection. Thus, the proposed method has a similar concept to the lab-on-a-chip approach, in which an electric device that combines one or more functions on a single integrated circuit (chip) provides highly sensitive or high productivity analysis of chemical or biological processes.

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