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Improved speed of hydrogen detection by Schottky diodes on InP with electrophoretically deposited Pt nanoparticles and graphite contacts

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ABSTRACT

The electrophoretic deposition (EPD) of nanoparticles (NPs) of the catalytic metal platinum (Pt) onto semiconductor wafers of indium phosphide (InP) from colloid solution in isooctane was studied at room temperature. The colloid solution for EPD was prepared by the chemical reduction of water solutions of the metal salts, confined to AOT reverse micelles in isooctane with hydrazine reducing agent. Four EPD-cast samples of Pt NPs were prepared on polished n-type InP wafers with varying times of deposition. The sheet density of Pt NPs varied from approximately 10% coverage of the substrate to 100% coverage of the substrate by several monolayers of Pt NPs, as observed by SEM. EPD was performed on a masked surface, enabling to make separated small deposited spots. Schottky contacts were made on the deposited spots by printing the contacts with colloidal graphite. The time response of the current to a 0.1% hydrogen exposure exhibited a continuous increase of saturation current and a decrease of the response time with increasing Pt NPs sheet density. Layers of Pt NPs were also prepared on p-type InP wafers. The current of the p-type InP diodes was observed to decrease with the exposure to hydrogen; its decrease was much smaller than the increase of current in n-type InP diodes. This demonstrates that two mechanisms are involved in formation of the hydrogen dipole layer. We have suggested the increase in hydrogen affinity by correlation effects as the second mechanism added to the well known hydrogen polarization by the electric field of the Schottky barrier.

1. Introduction

Sensitive and fast-responding hydrogen sensors must be installed in the environment where hydrogen may appear in concentrations above 4% because of its high inflammability in air, causing destructive explosions. Besides, they are used in various workflows as parts of production processes. Useful is their application in hydrogen leak testers using nonflammable hydrogen/nitrogen mixtures [1], which can be much cheaper than their helium-based counterparts. The number of hydrogen sensor publications has been growing exponentially since 1976 [2].

Hydrogen sensors based on semiconductor technology are of low cost, small size, long-term reliability and can be easily integrated into electronic networks. A review of Schottky barrier hydrogen sensors is given in [3]. For hydrogen detection by this type of device, some catalytic metal, usually Pd or Pt, is used. Hydrogen molecules are dissociated into hydrogen atoms on the catalytic metal and adsorbed on the semiconductor–metal interface. They are polarized and form a dipole layer, which changes the Schottky barrier height (SBH). This, in turn, can be measured by the change of current–voltage or capacitance–voltage characteristics.

Various n-type semiconductors were used for fabrication of Schottky barrier hydrogen sensors with Pd or Pt metals, including n-type InP semiconductor with Pt metal [4,5]. The last one is similar to this paper; except that we use separated Pt metal nanoparticles (NPs) coated by a non-metallic nanolayer instead of an intimate-contact of Pt metal. Usually, room temperature Schottky barrier hydrogen sensors with Pd or Pt catalytic metals on n-type inorganic semiconductors have high sensitivity, performance in wide range of hydrogen concentrations, good reproducibility and reliability, good temporal stability, small size and low cost. They also are sensitive to hydrocarbons that are dissociable with catalytic metals; however, their sensitivity to hydrogen is much higher [5]. Reported diodes have all specified characteristics. Despite of many published papers dealing with Schottky barrier hydrogen sensors, not much is known about the detection mechanism. Three crucial parameters of hydrogen detection exist: sensitivity, response time, and recovery time to be elucidated and handled. The main goal of this paper is to contribute in this course, in particular in the effort to shorten the response time at extremely low, yet detectable, hydrogen concentrations observed in our previous studies published recently [6–10].

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Improvement of response time to exposure of hydrogen/nitrogen mixtures by increasing density of catalytic metal nanoparticals in hydrogen sensors is the main goal of the study. The resulsts can be practically applied in hydrogen leak testers [1].

2. Experimental

Colloid solutions of Pt NPs in isooctane were prepared by reducing water solutions of Pt salts, enclosed in reverse micelles formed with the surfactant sodium di-2-ethylhexysulfosuccinate (AOT) [11]. Reagent grade chemicals were purchased from Sigma–Aldrich. The Pt NPs in prepared colloid solutions were monitored by surface plasmon resonance peaks in UV–VIS optical spectrum using spectrophotometer SPECORD 210 of Analytic Jena, Germany. The spherical shape of Pt NPs with monodispersed diameter of about 5 nm was determined by scanning electron microscope (SEM) JEOL JSM-7500F, Japan using samples obtained by evaporation drops of the colloid solution on the graphite-covered microscopic grid (not shown).

Intentionally undoped, one-side-polished wafers of n-type InP single crystals, with donor density 10^{16} cm^{-3}, were purchased from Wafer Technologies (Milton Keynes, UK). P-type InP single crystal ingots with Zn acceptor density 10^{17} cm^{-3} were grown by Czochralski technique (LEC). Wafers of 1 mm thickness cut from the ingots were lapped on the both sides and processed on one side by chemo-mechanical polishing. Samples 1 cm × 1 cm were cleaved from a wafer. A sample was washed in pure boiled methanol and dried quickly in a flow of pure air. The unpolished side of the sample was provided with an ohmic contact at room temperature by rubbing liquid gallium and the contact was pasted with commercial conductive silver paint on the cathode in a cell for electrophoretic deposition (EPD). The cell was rinsed several times with pure isooctane, filled with pure isooctane, connected to the voltage source of 1000 V and the current was tested. That was repeated until the minimum current was reached. Then the cell was filled with 1 ml of the colloid solution of Pt NPs in isooctane. The EPD was conducted with a 100 V voltage, keyed with a time period of 100 ms and a 50% duty-cycle (keyed EPD). The deposition time was varied from 15 min to 27 h. The graphite plane-parallel anode in the Teflon-made EPD cell was separated by 1 mm from the polished side of the sample. When the deposition time ended, the colloid solution was poured out; the sample was quickly rinsed with isopropyl alcohol to prevent additional deposition by evaporating isooctane from the colloid solution remaining on the surface. The deposited surface was observed by SEM.

Schottky contacts were prepared by touching the Pt NPs deposited surface with a Teflon point, dipped in a water-based colloidal suspension of graphite (Agar Scientific), and allowing the contacts to dry at room temperature (22 °C) at a relative humidity of 40%. Such Schottky contacts were used for the study of samples with sparse Pt NPs deposition, obtained with shorter deposition times. The surface of the sample, intended for dense Pt NPs deposition, was masked in advance by painting an appropriate pattern with acetone nail varnish. Thus, only unmasked positions on the surface were covered with Pt NPs by EPD, and the graphite Schottky contacts were painted onto said locations. Each diode consisting of the graphite Schottky contact and the opposing ohmic contact was studied by measuring current–voltage characteristics (*I*–*V*) as a function of exposure to ambient hydrogen. The *I*–*V* were measured by Current–Voltage Source-Measure Unit 236 (Keithley, Cleveland, OH, USA) controlled by a PC computer using LabView-based software. The sensitivity to hydrogen was determined on the same equipment by measuring current at constant voltage as a function of time alternatively in the flow of hydrogen mixed in nitrogen carrier gas and in the flow of air. A calibration mixture of 0.1% hydrogen/99.9% nitrogen was purchased from Linde Gas Company, Germany. For the measurement with other hydrogen concentrations in the range from 10^{-4}% (1 ppm) to 0.1% of hydrogen, the calibrated mixture was further mixed with pure nitrogen by using gas flow meters and controllers (Bronkhorst High-Tech, Ruurlo, Netherlands).

3. Results and discussion

Four wafers of n-type InP, marked (1), (2), (3) and (4), were used for keyed EPD of Pt NPs with the voltage 100 V, period 100 ms and 50% duty-cycle using four different deposition times; 15 min, 1 h, 4 h and 27 h, respectively. SEM images of the deposited wafers are seen in Fig. 1.

The SEM image of sample (1), which corresponds to a 15 min deposition, consists of approximately 40 individual Pt NPs distributed across the imaged region. These nanoparticles are spaced far from each other. The image of sample (2), which corresponds to a 60 min deposition, consists of approximately 150 Pt NPs that are four times more densely packed than the nanoparticles in the image for sample (1). We assert that the fourfold increase in density can be attributed to the fourfold increase in deposition time. Sample (3) comprises a film produced from a 240 min deposition; about 600 Pt NPs in this sample are primarily aggregated into small clusters. Notably, the density of NPs in sample (3) is four times larger than that seen in the image of sample (2).

This suggests that during EPD, the first deposit is cast randomly across the surface or occupies locations on the surface that are particularly attractive to the NPs. Thereafter, the presence of "seed" NPs on the surface tended to attract additional NPs to those locations. This distribution drove the formation of the observed clusters [12,13]. The formed clusters, which agglomerate not only in the surface plane but also orthogonal to the surface, necessitate additional NPs to cover the surface, compared to the case of NPs deposited only onto the planar surface.

Fig. 2 shows a SEM image of keyed EPD with shorter time period of 2.5 ms. The 1 h deposition time and all other parameters of EPD (except the period) were the same as for sample with the image shown in Fig. 1 (2). Comparing Figs. 2 with 1 (2), a difference between the two depositions is evident, given the two different keying periods 2.5 ms and 100 ms. Obviously, the deposition with the shorter period of keying 2.5 ms produced many more clusters (Fig. 2) than the deposition with the longer period 100 ms, shown in Fig. 1 (2). The average density (i.e. the number of particles per square) of Pt NPs in Fig. 2 is much larger than the one in Fig. 1 (2); the density is similar as the one in Fig. 1 (3), which was deposited four times longer. Also, the average size of the Pt NPs in Fig. 2 is smaller than their size in Fig. 1. This disparity in deposited NP diameter suggests that a larger number of smaller NPs (due to their electrophoretic mobility) were addressed by EPD electric field when a shorter period of keying and more mono dispersed deposits were employed. Thus, the smaller NPs were selected from the EPD suspension, due to their higher electrophoretic mobility, by keying with a higher frequency. In image (4) in Fig. 1 (4) (27 h deposition), the InP surface is fully covered with Pt NPs. The thickness of the Pt NPs layer was imaged in cross-section by SEM (Fig. 3). The thickness of the film is greater than 150 nm. This supports our observation of additional lateral electrical conductivity due to deposited Pt NPs. (In the first three cases no additional lateral conductivity was observed.) Due to the lateral conductivity of long-time Pt NPs depositions, the wafer (4) was masked with a grid, leaving separated small areas for EPD.

Forward and reverse *I*–*V* of the best Schottky diodes measured on wafers (1), (2), (3) and (4) are shown in Fig. 4. All diodes have high rectification ratios, from 6 to 8 orders of magnitude at the