Sensors and Actuators B 165 (2012) 104–109

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Schottky barriers on InP and GaN made by deposition of colloidal graphite and Pd, Pt or bimetal Pd/Pt nanoparticles for H_2-gas detection

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ARTICLE INFO

Article history:
Received 25 October 2011
Received in revised form 18 January 2012
Accepted 9 February 2012
Available online 17 February 2012

Keywords:
Metal nanoparticles
Electrophoretic deposition
Schottky diodes
Schottky-Mott limit
Hydrogen detection
Gas sensors

ABSTRACT

The paper reports on InP and GaN Schottky diode hydrogen sensors prepared by printing colloidal graphite on InP and GaN with catalytic metal Pd, Pt or bimetal Pd/Pt nanoparticles (NPs), electrophoretic depositions of metal NPs on surfaces of semiconductor wafers were performed from isooctane colloid solutions prepared by reverse micelles technique with dioctyl sodium sulfosuccinate (AOT) surfactant. Deposited metal NPs were characterized by SEM. Current voltage characteristics of the diodes showed high rectification ratio (about 10^7 at voltage 1 V), low leakage currents and high Schottky barrier heights giving evidence of small Fermi level pinning. Currents changed by more than six orders of magnitude after diode exposures to 0.1% hydrogen in nitrogen, showing extremely high sensitivity of hydrogen detection. Time response of the current of forward voltage biased diodes to exposure of various concentrations of hydrogen in nitrogen was measured in the range from 1 to 1000 ppm of hydrogen. The detection limit of hydrogen was estimated at 0.5 ppm.

1. Introduction

Hydrogen (H_2) gas has been used in various places of human activities, in industry, medicine, research and newly also for automotive purposes and in perspective H_2 economy. However, H_2 is a flammable gas, explosive with air at low concentrations of 4%. As H_2 consists of small molecules and is stored in containers at high pressure, it can leak easily to the environment. Thus, it is advisable to install sensitive and fast response H_2 detectors in all places where H_2 gas is stored for well-timed warning against the danger of explosion. Besides, H_2 can be favorably used as a tracer gas for leak detection instead of helium [1]. Development of high-performance miniature H_2 sensors with low energy consumption is important. Therefore, H_2 sensors have been still extensively studied. Among various types of H_2 sensors those based on semiconductor Schottky barriers were the most sensitive and easily integrable with novel electronics. In them, catalytic metals palladium (Pd) or platinum (Pt) were employed for dissociation of H_2 molecules as the necessary means for H_2 response. There has been already reported a number of Pd and Pt Schottky diode gas sensors on InP or GaN semiconductors [2–24]. Among them, H_2 sensors with Pd or Pt in the form of nanoparticles (NPs) have been shown to exhibit enhanced sensing response.

The paper reports on Schottky diode H_2 sensors prepared by printing colloidal graphite on polished surfaces of n-InP or n-GaN wafers with sub-nanolayers of Pd, Pt or bimetal Pd/Pt(2:1) NPs previously deposited. The NPs were deposited electrophoretically from colloid solutions prepared by hydrazine-chemical-reduction of metal-salts-water-solutions caged in reverse micelles dispersed in isooctane [25–27]. The paper is closely related to our previous studies published recently [28–31]. While the time response of InP sensors to various H_2 concentrations has been already published in our previous paper [30], the response of GaN sensors is the object of this paper.

2. Experimental

Intentionally not doped semiconductor wafers of n-InP and n-GaN, polished on one side, were obtained from Wafer Technology and Kima Technologies, respectively. Pure chemicals for preparing colloid solutions by reverse micelle technique [25–27] were purchased from Sigma Aldrich. Water solution of colloidal graphite for printing Schottky contacts was obtained from Agar Scientific.

Colloids with catalytic-metal NPs were prepared by reverse micelle technique according to Ref. [3]. Acidic salts of Pd or Pt were reduced by hydrazine in reverse micelles of water-AOT-isooctane at room temperature. For preparing bimetal NPs the mixture of Pd and Pt salts in the molar ratio 2:1 was used. The molar ratio of water to AOT was made 5 with the concentration of AOT 1 M. The concentration of metal salts was 0.1 M and that of hydrazine 1 M. The metal NPs obtained in this way were spherical, mono-dispersed

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doi:10.1016/j.snb.2012.02.023

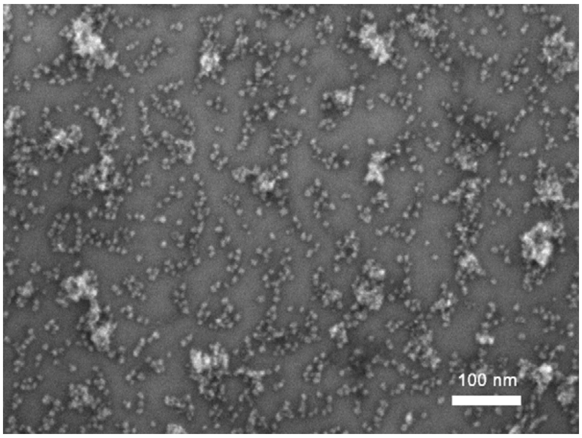

Fig. 1. SEM image of GaN surface with Pt nanoparticles. The scale 100 nm is shown with the bright bar at the bottom of the image.

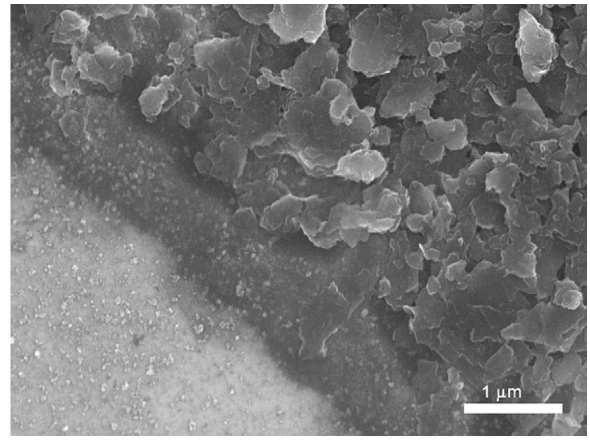

Fig. 2. SEM image of GaN surface with graphite contact on the right and with Pt nanoparticles seen on the left. The scale 1 μm is shown with the bright bar at the bottom of the image.

with the diameter 7 nm as imaged by scanning electron microscope (SEM) of Jeol JSM-7500F. Optical absorption due to surface plasmon resonance of metal NPs in the colloid solution was observed by split-beam UV-VIS spectrophotometer SPECORD 210 of Analytic Jena.

Electrophoretical deposition was provided at room temperature in specially constructed tightly sealed Teflon cell to prevent leakage of the volatile isooctane solvent of the colloid solution [32]. Just before starting deposition, wafers were cleaned in boiled pure methanol for 3 min. Each wafer was provided with ohmic contact on one side and fixed by this side with colloidal silver paint to the negative electrode (cathode) in the electrophoretic cell, so that the opposite plane-parallel graphite electrode was 1 mm apart from the polished plain side of the wafer. For the deposition of metal NPs, 10 Hz period keyed voltage with duty cycle 1 was applied for 1 h. To make Schottky contacts, several small area (0.075 mm^2) circular spots were printed with colloidal graphite on the wafer surface electrophoretically deposited with metal NPs. Each of that contact formed a Schottky diode with the ohmic contact on the other side of the wafer.

The deposited metal NPs and the printed graphite contacts were imaged by SEM. The prepared Schottky diodes were measured at room temperature by current–voltage-characteristics and by current–time-response of voltage biased diodes to the flow of H_2-nitrogen blends (H_2/N_2) followed by time-recovery in the flow of air. Reproductivity of performances of the diodes was very good; it depended on the homogeneity of the InP or GaN crystal materials and surface polishing.

3. Results and discussion

The SEM image of Pt NPs deposited electrophoretically on GaN surface can be seen in Fig. 1. The NPs were deposited on the nitrogen-side of the GaN wafer, oriented perpendicularly to the *c*-axis. It is patent that a sub-monolayer of NPs was formed at the conditions. The Pt NPs were circular, nearly mono-dispersed with the average diameter 7 nm.

Graphite contact on GaN surface can be seen in the SEM image with smaller magnification in Fig. 2. The graphite is seen in the upper-right area of the image while the lower-left area is the surface partly covered with Pt NPs. The darker stripe in between was probably formed during contraction of the graphite contact by evaporating water solvent of colloidal graphite and it may be caused by surfactant remains. Otherwise, the graphite contact consists of irregular grains of the average size below 1 μm. The thickness of the graphite contact, measured by a micrometer was estimated at 20 μm.

Qualitatively equal images as in Figs. 1 and 2 were obtained with the other sub-monolayers of Pd or Pt NPs deposited electrophoretically on InP and GaN wafers.

Current–voltage characteristics of six kinds of graphite diodes with depositions of sub-monolayers of Pd, Pt or bimetal Pd/Pt NPs on InP or GaN are shown in Fig. 3. Forward biased characteristics have currents many orders of magnitude larger than reverse biased characteristics at voltages above 1 V, which shows on high quality of the diodes, with small leakage currents. Each forward characteristic, in the semi-logarithmic scale, consists of two parts, a quasi-linear curve at lower voltages and an exponential-decay-like curve at higher voltages caused by the series resistance of the diode.

The quasi-linear curve reflects the electron transport over the Schottky barrier and it can be used to estimating the value of barrier

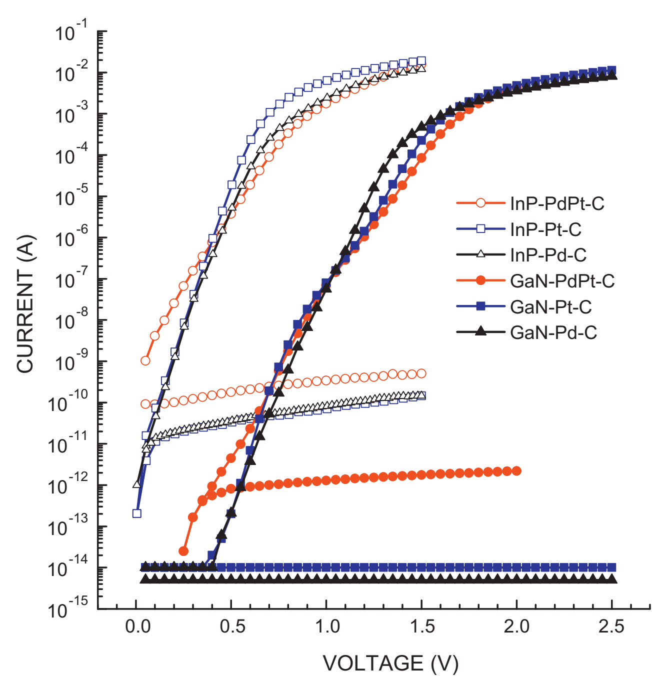

Fig. 3. Forward (up) and reverse (down) current–voltage characteristics of six Schottky diodes prepared on InP and GaN wafers with Pt, Pd and Pd/Pt nanoparticles. Self-explaining assignments are shown by the labels.