FILMS OF METAL NANOPARTICLES DEPOSITED ON SEMICONDUCTORS BY ELECTROPHORESIS: TECHNOLOGY AND CHARACTERIZATION

Karel ZDANSKY, Jiří ZAVADIL, Pavel KACEROVSKY, Frantisek KOSTKA, Jan LORINCIK, Ondrej CERNOHORSKY, Martin MULLER, Martin KOSTEJN, Anton FOJTIK

a Institute of Photonics and Electronics AV CR, Praha, CR, zdansky@ufe.cz
b Faculty of Nuclear Sciences, Czech Technical University, Praha, CR, ftk@troja.fjfi.cvut.cz

Abstract

Layers of nanoparticles in micelle enclosures were deposited on InP substrates by electrophoresis from isooctane colloid solutions containing Pd or Ag nanoparticles. The layers were investigated by SIMS, low-temperature photoluminescence spectroscopy and topography, absorption spectroscopy, Raman spectroscopy and sensitivity to hydrogen. Photoluminescence of InP was enhanced by the layers of Pd or Ag nanoparticles. Schottky barriers made on the n-type InP with layers containing Pd nanoparticles showed significant sensitivity to hydrogen in contrast to those containing Ag nanoparticles.

1. INTRODUCTION

A structure formed by a layer of separated metal nanoparticles deposited on the surface of a semiconductor macromaterial shows similar physical properties as the cognate structure formed by an integral metal macromaterial layer. However, the two structures can be considerably different in certain aspects. In particular, optical radiation can penetrate through a layer of metal nanoparticles much easily than through an integral metal layer. In the case of metal nanoparticles in a nonconducting cover, e.g. surfactant, the nanoparticles are farther apart and the radiation penetration is more effective. The penetrated radiation can induce photoluminescence (PL) or photovoltage responses in the semiconductor. More than that can appear. In addition, metal nanoparticles can even amplify the responses. The amplification is caused by the electron motion induced by the impacting radiation in metal nanoparticles. This synchronous electron motion generates secondary electromagnetic field leading to the amplification of the original one. Thus, we can regard the metal nanoparticles as antennas amplifying the impacting and emitting radiations [1]. Quantum mechanical analysis taking into account interactions between surface plasmons in metal nanoparticles and the nearby electron states on the semiconductor surface shows on a strong coupling between them [2]. A study of the coupling is important for the gaining a new basic knowledge as well as for practical applications in electronics and optoelectronics. Enhancement of photovoltage will enable fabrication of more efficient solar cells or photodetectors of higher quality. Light emitting diodes and semiconductor lasers of higher performance can be obtained by the luminescence enhancement. Also, it was shown recently that the intensity of Raman spectra was enhanced by metal nanoparticles [3]. Moreover, ordered arrays of such metal nanoparticles on semiconductors can form structures of novel properties. Potential regions to exploit such structures are in films for Raman scattering, selective solar absorbents, photovoltaic cells, optical gratings, antireflection surface coatings, photoluminescence
devices, diodes, sensors, nanostructure electrodes, chip electric converters, as well as data storages and microelectronic devices.

Metal nanoparticles can be heated to pretty high temperatures when they are illuminated with the light of the wavelength of plasmon resonance [4]. This effect is used e.g. for treatments of tumor disease. In the case of a semiconductor structure with deposited metal nanoparticles, this effect can be used for selective heat treatments of materials in the proximate environment for its transformation such as phase transitions.

A semiconductor forms a Schottky barrier at the interface with a layer of metal nanoparticles analogously as with the macroscopic metal layer. When common technologies of metal deposition are used the semiconductor surface is disturbed and electron surface stated with a high density are created. Disturbances arise partly by the impact of metal atoms during deposition and partly by stresses between the deposited metal layer and semiconductor due to the lattice mismatch or eventually by a chemical reaction of the metal with the semiconductor. The surface states cause Fermi level pinning on the semiconductor surface in the position of the maximum electron state density which presents fixing of the Schottky barrier height. Thus the barrier height is independent of the kind of the used metal which limits exploitation of barrier height chances for electronic devices. It is in particular true in the case of a low barrier when its rectification properties are lost. Creation of surface states is strongly reduced in the case of a Schottky barrier made from metal nanoparticles. First, practically no stress between the semiconductor and the layer of metal nanoparticles occurs because the bindings among the nonoparticles are weak and they easily adjust their positions to the lattice of the semiconductor surface. Chemical reaction between the semiconductor and the metal is prevented when the metal nanoparticles are enclosed by a surfactant which does not react with the semiconductor. Finally, e.g. during electrophoretic deposition of nanoparticles from a colloid solution, the impact energy of nanoparticles is very small and does not disturb the semiconductor surface.

Surface of some semiconductors is much sensitive to the disturbance so that it is hard to prevent creation of surface states during preparation of Schottky barriers by conventional methods. The InP is just such a semiconductor. Schottky barrier height on n-type InP is usually too small with practically no rectification ability at room temperature. In contrast, Schottky barrier on the same material made from metal nanoparticals by electrophoretic deposition was found as high as 1 eV having excellent rectification properties [6]. On the n-type InP with Pd nanoparticles deposited electrophoretically hydrogen sensors were prepared which had much better performance than sensors prepared by other methods on the same materials [7].

The method of electrophoretic deposition of nanoparticles is steadily gaining more attention in the science and technology of solid state materials [8]. The method lies in the process when electrically charged nanoparticles dispersed in a non-polar liquid mediums in the form of colloid solution are drifted by the electric field to the sample placed on an electrode where they give up the electric charge and form a relatively firm and homogeneous layer. Theoretical simulation of the process of electrophoretic deposition shows on its fine line with molecular beam epitaxy [9]. Successful deposition requires preparation of a stable colloid solution with electrically charged nanoparticles with small spread in shape and size, dispersed in a proper non-polar solvent where is provided active mechanism preventing their coagulation and agglomeration. Charge incorporation in nanoparticles is
accomplished by simultaneous interplay of a number of physical chemical mechanisms [10-12]. The actual polarity of the charge of metal nanoparticles in an particular experiment is to be determined empirically [13-15]

In this work we report on investigation of structures with Pd and Ag metal nanoparticles deposited electrophoretically on InP wafers from colloid solutions prepared by the method of reverse micelles in isoocctane.

2. EXPERIMENTAL

We have studied structures with thin films of metal nanoparticles deposited onto surfaces of n-type indium phosphide (InP) single crystals from colloid solutions. Single crystal ingots of InP were grown by Czochralski technique using MSR6R apparatus by Metal Research, Ltd from UK. Wafers cut from the ingot of 1 mm thicknesses were lapped to 0.5 mm and polished on the both sides chemical mechanically with a water solution of sodium chlorate by using MP5 machine by Logitech, Ltd. from UK. Samples of 10 ×10 mm$^2$ were shortly etched for 15 s in a hot solution of 0.2 % Br in methanol to remove a conducting surface arisen during the polishing. Samples were provided on one side with an all-area ohmic contact by rubbing liquid solution of tin in gallium at room temperature. Colloid solutions of metal nanoparticles in isoocctane were prepared by reverse micelle technique from water solutions of metal compounds and reducing agents. The shapes of metal nanoparticles in the colloid solution were monitored by a transmission electron microscope (TEM) and/or by scanning electron microscope (SEM) using films prepared by evaporating the isoocctane colloid solution on a microscopic metal mesh. Metal nanoparticles were spherical shape of 7 nm diameter with 10 % dispersion [6]. Optical absorption spectra due to surface plasmons of Pd and Ag nanoparticles in isoocctane monitored by a split-beam photo-spectrometer are seen in Fig. 1. The Ag nanoparticles are revealed by the peak at 420 nm. The Pd nanoparticles are revealed by the peak at 280 nm. The peak at about 220 nm is caused by absorption in the surfactant compound AOT. It is shifted to higher wavelength in the colloid solution with Pd nonoparticles due to a partial convolution with the peak at 280 nm.

To provide the electrophoretic deposition, an InP wafer was affixed by a conducting paint to an electrode in a tight-closing cell with a graphite plain-parallel opposite electrode 1 mm apart. The cell was filled with the colloid solution and the dc voltage of 36 V was applied via the resistor of 5 MΩ in series for 30 min. The current was monitored by measuring the voltage on the resistor. Some auxiliary depositions were made on glass substrates. For these the dc voltage 1400 V was applied giving about the same voltage on the resistor as with the InP. Some InP samples were masked before the deposition by the
acetone paint in about one half of the surface and the mask was removed by solving it in acetone. These samples were made to compare the results of certain measurements in both parts, one with the deposited layer of nanoparticles and the other without it. Several Schottky diodes were prepared by spotting silver conducting paint in several places on the InP wafer-side with the deposited layer and making a common ohmic contact on the other side of the wafer. The diodes were electrically separated because the lateral conductivity of the deposited layers was much smaller than their axial conductivity [13]. Forward and reverse current-voltage characteristics of the diodes were measured. The diodes were also tested for their sensitivity to hydrogen in a cell with a through-flow gas system. The deposited layers were characterized by SIMS, AFM, optical absorption or reflection spectroscopy, spectroscopic photoluminescence (PL) topography at room and liquid nitrogen temperature, PL spectroscopy at liquid helium temperature and Raman spectroscopy at room temperature.

3. RESULTS AND DISCUSSION

Depositions of nanoparticle layers were performed with InP samples placed on both, cathode and anode and the measurements of these two types of layers were compared. In both cases the layers were of about 100 nm thick after 30 min deposition; however, the properties of these two types of layers were different. SIMS spectra of layers deposited from the colloid solution with Pd nanoparticles on InP wafers placed on the cathode and on the anode are shown in Fig. 2. Palladium is revealed by five peaks on the scale of atomic masses 104, 105, 106, 108 and 110 with relative intensities 11:22:37:24:12 corresponding to the natural abundances of palladium isotopes. The intensity of palladium mass spectrum is about two orders of magnitude larger in the layer deposited on the anode than in the layer deposited on the cathode. It shows that the Pd nanoparticles in the colloid solution are either predominantly or altogether negatively charged.

We can suggest that palladium nanoparticles behave like anions in the colloid solution in contrast to palladium ions in water solutions of palladium salts which act as cations.

This suggestion can be confirmed by the measurement of the sensitivity to hydrogen. The current of the diodes biased with reverse voltage 0.9 V increased when the flow of the gas mixture of...
hydrogen and nitrogen was switched on and decreased back to the original value when it was changed to the flow of air. The increase of the order of two magnitudes can be seen in Fig.3. In the case of the diode prepared on the InP wafer with the layer of nanoparticles deposited on the cathode from the same colloid solution with Pd nanoparticles no change of current was observed. Two assumptions have to be made to explain the difference. First, the layer deposited on the anode contains palladium nanoparticles. Second, palladium nanoparticles dissociate hydrogen molecules. Then, hydrogen ions can diffuse to the surface of InP and form a charged double layer which reduces the height of Schottky barrier leading to the increase of the measured current. It confirms the suggestion made on the results of SIMS that Pd nanoparticles are negatively charged. Moreover, it allows suggestion that hydrogen dissociation is needed for sensing hydrogen by Schottky barriers.

Let us look at the results of photoluminescence measurements. For that purpose InP samples with nanolayer deposited on about one half of the surface were used. The photograph of such an InP wafer in Fig. 4 shows the painted mask preventing the deposition of nanoparticles on the InP surface on the right hand side of the wafer. PL spectra measured at 4 K with excitation by He-Ne laser on InP with Pd nanoparticles, deposited on the anode from the colloid solution containing Pd nanoparticles. The spectrum marked as InP was taken from the uncovered part and that marked as InP-Pd from the part covered by nanoparticles.

Fig. 4. InP wafer masked by paint on the right hand side. The rectangle drawn in the centre part shows approximately the area scanned by the PL topography.

Fig. 5. Two PL spectra measured at 4 K with excitation by He-Ne laser on InP with Pd nanoparticles, deposited on the anode from the colloid solution containing Pd nanoparticles. The spectrum marked as InP was taken from the uncovered part and that marked as InP-Pd from the part covered by nanoparticles.

Fig. 6. Raman spectrum of InP sample with the layer of nanoparticles deposited on the anode from the colloid solution with Pd nanoparticles (red line marked as InP-Pd) and the spectrum of InP without deposition (blue line marked as InP). The intensity of the later spectrum was multiplied by the factor of 50 for better visualization.

Fig. 6. Raman spectrum of InP sample with the layer of nanoparticles deposited on the anode from the colloid solution with Pd nanoparticles (red line marked as InP-Pd) and the spectrum of InP without deposition (blue line marked as InP). The intensity of the later spectrum was multiplied by the factor of 50 for better visualization.
conduction band and shallow acceptors. The band marked as BE is caused by radiative recombinations of bound excitons. The B-A band is more than twice stronger when emitted from the surface covered with the film of Pd nanoparticles than that emitted from the clean InP surface. It can be explained by the enhancement due to the interaction between surface plasmons of Pd nanoparticles and the electron states in InP near the surface. No similar enhancement was observed on InP samples with layers of nanoparticles deposited on the cathode from the same colloid solution.

Further, we measured Raman spectra on InP samples with deposited nanoparticles and compared their intensities with those measured on InP without deposition. In Fig. 6, there is seen the spectrum taken on the InP sample with the layer of nanoparticles deposited on the anode from the solution with Pd nanoparticles (red line) and the spectrum taken on InP without deposition (blue line). The intensity scale of the blue line spectrum was multiplied by 50 to reach about the same heights of both spectra. It means that the Raman intensity was enhanced about 50 times by the layer of Pd nanoparticles. No similar enhancement was observed on the InP samples with layers of nanoparticles deposited on the cathode from the same colloid solution. This observation further confirms that Pd nanoparticles in the colloid act as anion-like particles.

Further, we performed electrophoretic depositions from the colloid solution with Ag nanoparticles on InP wafers placed on the cathode and on the anode. Besides, analogous depositions were performed on glass substrates. Optical reflection spectral measurements provided on the InP wafers showed peaks corresponding to Ag surface plasmons on samples with nanoparticles deposited on the cathode while the peaks on the samples deposited on the anode were much weaker, on the edge of differentiability [15]. Similar results were obtained on the glass samples. They were measured by optical absorption spectroscopy. Peaks of optical absorption due to Ag plasmons were observed on samples with nanoparticles.
deposited on the cathode while no such peaks were observed on the samples deposited on the anode [15]. It suggested that, in contrast to Pd nanoparticles, Ag nanoparticles act like cations, bearing a positive charge in the colloid solution. This suggestion will be confirmed in the following.

PL spectra measured at 4 K with excitation by He-Ne laser on InP with Ag nanoparticles deposited on the cathode from the colloid solution containing Ag nanoparticles is shown in Fig. 7. There are seen two PL spectra of InP, one emitted from the clean surface of InP (blue line marked as InP) and the other emitted from the surface of InP covered with Ag nanoparticles (red line marked as InP/Ag). Each spectrum consists of two peaks, marked BE and B-A. The intensity of both PL peaks is more than twice stronger when emitted from the InP surface covered with the layer deposited on the cathode than that emitted from the clean InP surface. It can be explained by the enhancement due to the interaction between surface plasmons of Ag nanoparticles and the electron states in InP near the surface. No similar enhancement was observed on InP samples with layers of nanoparticles deposited on the anode from the same colloid solution of Ag nanoparticles.

Layers of nanoparticles deposited from colloid solutions with Ag nanoparticles on masked InP wafers were measured by PL topography at room temperatures and at temperature of liquid nitrogen. The scanned area embodies both parts, that covered with the layer of Ag nanoparticle and the clean InP surface as it is shown approximately in Fig. 4. In Fig. 8, there are two PL topographs of InP wafer covered with Ag nanoparticles on the left hand part and on the uncovered InP on the right hand part. The border between the two parts is indicated by the dashed line. The upper graph shows results of the measurement at room temperature, the lower graph those at liquid nitrogen temperature. The colour scale of PL intensity is shown on the right side of each graph. It is obvious that higher PL intensities appear in uncovered part of the InP wafer when measured at room temperature. However, they appear in the covered part when measured at liquid nitrogen temperature. It shows that the enhancement of PL intensity by Ag nanoparticles depends on the temperature. Small reduction of PL intensity at room temperature can be explained simply by shielding of the InP surface which is not overcome by the effect of the enhancement. The reduction of the enhancement shows on the reduction of the interaction between surface plasmons and InP electron states by the temperature. It is in agreement with the above reported result of PL measurements at 4 K which showed the enhancement by the factor of two, while at liquid nitrogen temperature the enhancement factor is only about three halves. Finally, it should be said that no enhancement of PL topography, only reduction independent of temperature, was observed on the InP wafers deposited by nanoparticles on the anode from the same colloid solution with Ag nanoparticles.

We sugest that low-temperature PL enhancement is caused by collective plasmon modes of metal nanoparticles arranged on the InP surface. The modes can be excited at low temperature and are coupled to electron states near the surface of InP. Stronger lattice vibrations at higher temperature disturb coherency of plasmon modes and thus reduce their interaction with electron states of the semiconductor. The interaction may depend on the type of the excited mode and different electron states may be coupled with different modes. It can explain why both PL peaks, BE and B-A are enhanced with Ag nanoparticles present (Fig. 7) and only one peak, B-A is enhanced with Pd nanoparticles (Fig. 5).
4. CONCLUSIONS

In the context with research of semiconductor gas sensors, layers of Pd and Ag nanoparticles were deposited by electrophoresis on InP and glass substrates. Their properties were consistently explained on the basis of SIMS, optical spectroscopy, current-voltage characteristics and hydrogen sensing measurements. Photoluminescence of InP was enhanced by the layers of Pd or Ag nanoparticles at low temperatures. Intensity of Raman spectra was strongly enhanced at room temperature. Schottky barriers made on the n-type InP with layers containing Pd nanoparticles showed significant sensitivity to hydrogen in contrast to those containing Ag nanoparticles. It supports the proposition that dissociation of hydrogen is a necessary process for hydrogen sensing on the basis of Schottky barriers. We consider that layers of Pd nanoparticles can be successfully used for making fast, sensitive and small-dimension sensors on the basis of InP.

Acknowledgments

The work has been supported by the grant KAN 401220801 of Academy of Sciences CR and by Grant Agency CR, grant number 102/09/1037.

REFERENCES

