Au Nanoparticle Sub-Monolayers Buried between Magnetron Oxide Thin Layers

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Abstract. In this work, a versatile method to increase the optical response of the oxide nanostructures is proposed. It combines a magnetron deposition of oxide matrix with the thermal deposition and aggregation of metallic nanoparticles, allowing the preparation of wide band gap oxide heterostructures with buried plasmonic Au nanoparticles. Thin layers of Si/TiO2 and Si/NiO were deposited by reactive magnetron sputtering in a 2D nanostructure, followed by 2.5 nm gold layer thermal deposition and in N2 thermal annealing at 550 °C to induce the growth of the Au nanoparticles. Then Si/TiO2/AuNP and Si/NiO/AuNP were covered with TiO2 and NiO respectively. The reflectance maximum of the LSPR band appeared at around 700 ÷ 720 nm for both heterostructures. It was demonstrated that both Si/TiO2/AuNP/TiO2 and Si/NiO/AuNP/NiO heterostructures can enhance optical response in comparison with Si/TiO2 and Si/NiO. The results obtained indicate a broad prospect of using the formed structures in the field of integrated optoelectronic devices.

1. Introduction

In recent years, increasing attention has been paid to oxygen-containing semiconductor materials [1]. This interest is due to their wide distribution and the relative simplicity and breadth of the spectrum of methods for their formation. In optical applications, titanium dioxide plays a special role [2]. However, its widespread use is limited by the fact that the intrinsic absorption peak of the material is in the UV region. In addition to n-type semiconductor oxides, p-type oxides have attracted more and more attention in recent years. Among them, one of the most represented is the metal oxides of the iron group (oxides of iron, nickel and, less, cobalt). There are a large number of works showing the promise of using nickel oxide as active layers of electrochromic devices and gas sensors. However, its use is also limited by objective factors [3], [4].

The introduction of plasmon activators, for example, gold nanoparticles (AuNP), into the matrix of wide-gap material allows us to translate the edge of the fundamental absorption of the material into the visible region [5], [6] and even control the type and magnitude of the conductivity of the material [7].

In this paper, we propose the implementation of localized plasmon resonance (LPR) on gold hemispherical particles buried in a semiconductor oxide matrix. An analysis of the literature shows that such heterostructures turn out to be effective highly sensitive elements of optical sensors for
various purposes. The aim of this work was to obtain Si/TiO$_2$/AuNP/TiO$_2$ and Si/NiO/AuNP/NiO nanocomposite coatings active in the visible wavelength range.

2. Experimental details
A novel technique for manufacturing the plasmonic heterostructures (figure 1) were used. First, by using magnetron sputtering [8] TiO$_2$ and NiO layers of 80 nm each were deposited on the n-Si and p-Si wafers [5], [9]. Then, a 2.5-nm-thick Au layer was deposited onto TiO$_2$ and NiO surfaces by thermal evaporation, with extra annealing at 550 °C for 60 min. [7] to Au nanoparticle formation. The last step was AuNP overgrowth with TiO$_2$ or NiO layers with a thickness of 150 nm each. The conditions for the formation of structures given in table 1.

![Figure 1. Schematic of the formed optically active heterostructures.](image)

The structure of the samples were analyzed by scanning electron microscopy (SEM), using a JEOL JSM-7001F equipped with Energy Dispersion Spectroscopy (EDS) attachment Bruker XLash 6/30. Top-view and cross-sectional images were obtained using both secondary and backscattered electrons, respectively for morphology studies and atomic weight contrast of the Au NPs.

The structural analysis of the coatings was carried out in terms of the Raman Spectrometry. Raman Spectrometry were made with Horiba Jobin-Yvon LabRam HR800 instrument with 1800 gr/mm grating in the backscattering geometry. The incident beam of a 532 nm laser with maximum output 50 mW was focused onto a 2 µm target spot. The data were recorded in Raman shift range (100 ÷ 7000 cm$^{-1}$). To improve signal-to-noise ratio, the data were averaged over 10 or 20 measurements, thus full data acquisition process for each location took 10 through 20 seconds. All the spectra were calibrated using a standard Si sample. To eliminate the dark current contribution to the data, special ‘dark measurements’ were performed for each sample and the obtained curves were subtracted from ‘raw’ spectra recorded with the laser beam on.

| Parameter                  | TiO$_2$ Conditions | NiO Conditions | Au Conditions |
|----------------------------|--------------------|----------------|---------------|
| Power supply in RF mode, W | 300                | 50             | -             |
| Target                     | 3 inch Titanium 99,999 | 3 inch Nickel foil 99,999 | Gold foil 99,9 |
| Base/work pressure, mbar   | 6*10$^6$/1.5*10$^3$ | 6*10$^6$/1.5*10$^3$ | ambient       |
| Ar flow sccm/ O$_2$ flow sccm | 9/2               | 11/1           | N$_2$ atmosphere |
| Temperature, °C             | ambient            | ambient        | 550           |
The thickness and refractive index of the structures were measured using a laser ellipsometer Horiba Jobin-Yvon. A helium-neon (HeNe) laser with a wavelength of $\lambda = 638.2 \text{ nm}$ were used as a radiation source. The optical reflectance spectra of the samples were measured in a Shimadzu UV-2450 (PC) spectrophotometer. Current-voltage curves were measured using Keithley 2400 source meter under AM1.5 solar spectrum at 20 °C. Spectra of external quantum efficiency were recorded using equipment based on Solar Laser Systems M266 monochromator.

3. Results and discussion

Typical SEM images of the structures formed are shown in figure 2. There are two layers of oxide are, between which there is a clearly defined boundary. Below the boundary, the oxide layers are amorphous both in the case of Si/TiO$_2$/AuNP/TiO$_2$ and Si/NiO/AuNP/NiO heterostructures. Above the boundary, in both cases, the formation of a textured oxide layer is observed. EDS results for Si/TiO$_2$/AuNP/TiO$_2$ indicate the presence of O, Si, Ti, and Au. In the case of Si/NiO/AuNP/NiO, the EDS results shows the presence of O, Si, Ni, and Au. The refractive index of the oxide layers was 2.43 in the case of Si/TiO$_2$ and 2.26 in the case of Si/NiO, which reflects its significant porosity [10], [11].

![Figure 2. Top-view and cross-sectional images of fabricated heterostructures: (a) Si/TiO$_2$/AuNP/TiO$_2$ and (b) Si/NiO/AuNP/NiO.](image)

Raman spectra of the formed structures are shown in figure 3. In the case of Si/TiO$_2$, the formation of amorphous layers on a silicon substrate was observed (peak with a maximum of about 520 cm$^{-1}$). The addition of plasmon activators into Si/TiO$_2$ depicted in the appearance of additional TiO$_2$ peaks.

The first order Raman scattering of the stable TiO$_2$ rutile phase (space group D$_{4h}^{14}$) has four active Raman modes: $B_{1g}$, $E_g$, $A_{1g}$, and $B_{2g}$. The metastable TiO$_2$ anatase phase (space group D$_{2d}^{18}$) has six active Raman modes: $1A_{1g}$, $2B_{1g}$, and $3E_g$. The Raman peaks for the bulk structures are 144 cm$^{-1}$ ($E_g$), 197 cm$^{-1}$ ($E_g$), 399 cm$^{-1}$ ($B_{1g}$), 513 cm$^{-1}$ ($A_{1g}$), 519 cm$^{-1}$ ($B_{1g}$), and 639 cm$^{-1}$ ($E_g$) for anatase phase and 143 cm$^{-1}$ ($B_{1g}$), 447 cm$^{-1}$ ($E_g$), and 612 cm$^{-1}$ ($A_{1g}$) for the rutile phase [12]. The large width of the peaks indicates a low structural perfection of the layer [13]. Although the anatase phase has no good stability comparing to the rutile, it was widely used because the anatase structure exposed outstanding photocatalysis and sensitization properties [14]. An analysis of Raman spectra indicates a change in the structures absorption as a result of the plasmon activators addition to the titanium oxide matrix, which may indicate the manifestation of surface enhanced Raman scattering [15].

In the case of Si/NiO, no characteristic peaks of crystalline (1549 cm$^{-1}$, 2M) nickel oxide were observed. There were only peak at 515 cm$^{-1}$ (2M), corresponding to low-structured NiO [16]. That is, the formation of amorphous nickel oxide was observed. The introduction of plasmon activators slightly affected the Raman spectra of the samples. This may be due to the high shielding ability of nickel oxide [17].
Figure 3. Raman spectra of fabricated heterostructures.

The reflection spectra of the formed structures (figure 4) analysis indicates that the maximum of sensitivity to irradiation appears at 700 ÷ 720 nm, which corresponds to the position of the localized plasmon resonance peak of Au nanoparticles [18].

Figure 4. Reflection spectra of fabricated heterostructures.

The effect of lighting on the current-voltage (CV) characteristics of the formed structures were evaluated (figure 5). As it is seen from figure 5, a, CV dependence was a pristine $p$-$n$ junction between doped metal oxide and silicon wafer layers. The sign of the current depended on the type of oxide conductivity (for $p$-NiO, the current was negative, for $n$-TiO$_2$ it was positive). The absolute values of currents in the case of Si/NiO/AuNP/NiO were two orders of magnitude higher than in the case of Si/TiO$_2$/AuNP/TiO$_2$. In both cases, lighting increases current at voltages above 4 V up to 1.5/1 in the
case of Si/TiO$_2$/AuNP/TiO$_2$ and up to 1.3/1 in the case of Si/NiO/AuNP/NiO. At zero bias, the lighting did not lead to the current increase.

![Diagram](image)

**Figure 5.** Typical current-voltage characteristics taken under illumination and in the dark:
(a) across structures, (b) in-plane.

As it is clearly seen from figure 5, b, the CV characteristic taken in-plane of formed structures corresponded to a two connected towards each other p-n junctions. Probably it was upper layer of oxide and doped metal oxide and vice versa. In both cases, lighting increases reverse branch current at voltages above 1 V up to 5/1 in the case of Si/TiO$_2$/AuNP/TiO$_2$ and up to 1.3/1 in the case of Si/NiO/AuNP/NiO.

4. Conclusion

In this work, a technique for optically active nanocomposite structures consisting of an oxide matrix containing plasmonic NPs formation were demonstrated. The aim of the work was to validate the proposed methodology and study the optical and electrical characteristics of the plasmonic heterostructures Si/TiO$_2$/AuNP/TiO$_2$ and Si/NiO/AuNP/NiO. The structures coatings fabricated showed a maximum reflection in the red region of the spectrum, which corresponds to the plasmon resonanse region of gold nanoparticles. The resulting structures were characterized by satisfactory surface and through conductivity, the ratio of light and dark currents reached 5/1 in the case of Si/TiO$_2$/AuNP/TiO$_2$. In addition, Si/TiO$_2$/AuNP/TiO$_2$ heterostructures can be suitable as substrates for surface enhanced Raman scattering.

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