Study of the optical properties of a NiO / AuNP / NiO nanocomposite film transferred onto a transparent flexible substrate

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Abstract. In this work a technique for optically active nanocomposite structures consisting of an oxide matrix with plasmonic NPs were demonstrated. A nanocomposite film was formed on a silicon substrate by NiO oxide matrix sputtering and gold nanoparticles dewetting. Studies of the morphology, elemental composition, and structure of the nanocomposite using SEM, EDS, XRD methods are presented. The transfer of the film onto a polymer substrate made it possible to study the optical characteristics of the obtained structures. It is shown that formed nanocomposite coatings on a polymer substrate are highly flexible and exhibit excellent mechanical properties.

1. Introduction

The problem of operating the propagation of electromagnetic waves is attracting more attention. A possible approach to solving this problem is applying surface plasmon resonance. Surface plasmon resonance - a model describing the transmission of electromagnetic waves for geometrically isolated objects [1]. Plasmonic oscillations are sensitive to the properties of the environment in which they propagate. For example, a change in the refractive index of an environment leads to a shift in the resonance frequency. The implantation of plasmonic particles, for example, gold nanoparticles (AuNP), into a matrix made of a wide-gap material makes it possible to transfer the fundamental absorption edge of the material to the visible region [2]. It was shown [3] that such heterostructures can act as active sensitive elements of optical sensors for various purposes.

The most important characteristic of optically active heterostructures is their spectral characteristics of transmission, absorption, and reflection. However, current technologies for the layers of complex composition formation are focused on the applying of substrates that are opaque in the optical region (silicon, gallium arsenide). At the same time, the initial stages of growth are significantly influenced by the substrate material (elemental composition, structure, morphology). In this regard, an urgent task is to develop a technology for transferring the formed coating from a growth substrate to an optically transparent carrier. Furthermore, flexible devices are expected to meet the increasing demands for wearable and portable electronics. To produce flexible photoactive devices, both methods of a semiconductor film growth directly on a flexible polymer base [4] and methods of transferring a grown film from a single crystal substrate to a polymer base [5] are used.
In this work, we propose a method for material transfer to a base that is transparent in the optical range of the spectrum, implemented for Si / NiO / AuNP / NiO nanocomposite structures formed on silicon substrates, active in the visible wavelength range, by means of an SU-8 photoresist with high transparency in the range 0.35 - 1.2 μm [6].

2. Sample preparation

2.1. Material preparation

Nanocomposite films were prepared via a three-step method on monocrystalline p-type silicon substrates with an orientation of (100) (figure 1). At the first stage, a NiO film is deposited on the silicon surface by the methods of RF magnetron sputtering. The sputtering was carried out at a power of 50 W from a Ni target (foil 99.999) in an Ar / O₂ gas mixture at an operating pressure of 1.12 mTorr. The flow of Ar and O₂ gases was 11 and 1 sccm, respectively. The NiO thickness was 80 nm. Then, an Au coating with a thickness of 2.5 nm was formed on the oxide surface using thermal evaporation. AuNP was formed by dewetting at temperatures of 550 °C for 60 min. Such modes of nanoparticle formation ensure the distribution of particles with a predominant diameter of 10 nm [7]. The last stage was the overgrowth of AuNP with a 150 nm thick NiO layer using magnetron sputtering in the modes given above. For further research, the substrate was divided into chips 10X10 mm in size.

Figure 1. Schematic diagram of the nanocomposite film formation process

2.2. Transfer of nanocomposite to SU8

Nanocomposite films were transferred onto a polymer base. Photoresist SU-8 was chosen as the polymer base. The choice of the material was made by its high transparency in the range of 0.35 - 1.2 μm, excellent mechanical characteristics and the ability to form topology using typical photolithography operations. An SU-8 film with a thickness of 25 μm was deposited onto a silicon growth substrate by centrifugation. Subsequent wet chemical etching of the silicon substrate ensured the separation of the nanocomposite and its transfer to the polymer base. Silicon was etched in a 30% KOH solution at a temperature of 75 °C. At the same time, SU-8 demonstrated sufficient adhesion to the NiO surface and resistance to wet alkaline etching. After release, the film with the nanocomposite becomes curved (figure 2), which is caused by residual internal mechanical stresses in the NiO and SU-8 layers.
2.3. Sample characterizations

The structure of the nanocomposite films prior to transfer 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.

X-ray structural analysis of the samples was carried out on X-ray diffraction patterns obtained in step-scan mode at room temperature on a D8 Advance powder diffractometer (Bruker, Germany) with a vertical goniometer Θ-, focusing according to Bragg-Brentano, on β-filtered CuKα radiation (λ = 1.54178 Å, Ni-filter), with the registration of the diffraction pattern by a high-speed linear detector LynxEye (capture angle 3.2 °), in the angles 2Θ = 24-56 ° and 35-46 °, with a scanning step of 0.03 ° and accumulation time 0.2 s / step. Tube operating modes U = 40 kV, I = 40 mA. The X-ray diffraction patterns were processed using the Diffrac EVA software and the ICDD (International Center for Diffraction Data) PDF-2 database of powder X-ray patterns.

Structural analysis of the coatings was carried out by Raman spectroscopy on a silicon substrate. Raman Spectrometry were made with Horiba Jobin-Yvon LabRam HR800 instrument with 1800 gr/mm grating in the backscattering geometry. The incident laser beam with a wavelength of 532 nm and a maximum power of 50 mW was focused into a target spot of 2 μm. The data were recorded in the range of the Raman shift (100 ÷ 7000 cm⁻¹). To improve the signal-to-noise ratio, the data were averaged over 10 or 20 measurements, so the complete data collection process for each location took 10 to 20 seconds. A standard Si sample was used to calibrate all spectra. To eliminate the influence of the dark current on the data, special “dark light measurements” were performed for each sample, and the resulting curves were subtracted from the “raw” spectra recorded with the laser beam turned on.

The thickness and refractive index of the structures were measured using a Horiba Jobin-Yvon laser ellipsometer. A helium-neon (HeNe) laser with a wavelength λ = 638.2 nm was used as a radiation source. The optical spectral characteristics of the samples were measured on a Shimadzu UV-2450 (PC) spectrophotometer in the range of 350 – 1200 nm. To measure the spectral characteristics of the transferred nanocomposite layer, the film was fixed on an amorphous silica substrate to ensure the surface flatness.

3. Results and discussions

Typical SEM images of the structures formed are shown in figure 3. There are two layers of oxide with a clearly defined boundary. EDS results indicate the presence of O, Si, Ni, and Au. The refractive index of the oxide layers was 2.26, which indicates its significant porosity [10], [11]. The results of the XRD shown on figure 4. Below the boundary the formation of cubic NiO (Fm-3m, a = 0.417 nm) with (200) preferred orientation is observed. Above the boundary the formation of a textured oxide layer with preferred (111) orientation is uncapped. Formation of cubic Au (Fm-3m, a = 0.408 nm) with
preferred (111) orientation on the boundary were also detected. Gold particles acted as a catalyst for the formation of textured (111) nickel oxide layer under the same growth conditions as (200) lattices without Au inclusions. According to Raman investigations (figure 5) there were only peak at 515 cm\(^{-1}\) (2M), corresponding to low-structured NiO [16]. Introduction of Au slightly affected the Raman spectra of the samples.

Figure 3. Top-view (a) and cross-sectional (b) images of fabricated heterostructure Si/NiO/AuNP/NiO

Figure 4. Raman spectra of fabricated heterostructures.

Figure 5. Raman spectra of fabricated heterostructures.

The reflection spectra of the formed Si/NiO/AuNP/NiO structures (figure 6 dash black) indicates a maximum of reflection appears at 680 ÷ 700 nm, which corresponds to the position of the localized plasmon resonance of Au nanoparticles [11]. SU-8 films without nanocomposite coating show high transparency in the optical range (figure 6 dash red). The measured transmission and reflection spectra of the nanocomposite coating on the polymer film (figure 6) are in good agreement with the data obtained before the transfer, and also indicate the presence of a localized plasmon resonance peak of AuNP. The absorption dependence was obtained on the basis of the measured reflectance and transmission spectra.
Figure 6. Reflection, Transmittance and Absorption spectra of fabricated heterostructures.

The released film has been shown to be highly flexible, making it suitable for flexible electronics. However, the resulting film has a low tensile strength compared to other polymer coatings such as PMMA. The curvature of the film is due to residual internal stresses in the polymer and nanocomposite layers and is 0.23 mm$^{-1}$. No surface curvature is observed on SU-8 films without nanocomposite.

4. Conclusion
In this work, a technique for optically active nanocomposite structures consisting of an oxide matrix containing plasmonic NPs formation were demonstrated. The transfer of the film onto an optically transparent substrate made it possible to study the optical characteristics of the formed films. The films produced showed the maximum reflection in the red spectral region corresponding to the plasmon resonance region of gold nanoparticles. Formed nanocomposite coatings on a polymer base are highly flexible and show good mechanical properties. The developed technology is relevant as reference samples for further work on the creation of flexible highly efficient electro-optical converters based on wide-gap semiconductors with plasmonic nanoparticles.

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