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Effect of noble metal nanoparticles in transition metal oxide magnetron sputtering

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Abstract. The purpose of this work is to study the transition metal oxides with metal nanoparticles structures formation features. A design technology is proposed, consisting of the oxide matrix magnetron sputtering, noble metal nanoparticles thermal evaporation and dewetting, and covering it with oxide. Gold nanoparticles, nickel and titanium oxides were used as materials under investigation. Metal-induced catalytic growth of nickel and titanium oxides on gold nanoparticles has been found. It is shown that the top layer being formed has a pronounced texture. During the process, cones are formed with an opening angle of 10—12° and a predominant growth direction coinciding with the crystallographic axis perpendicular to the (111) surface. The optical and electrical characteristics of the formed coatings were studied. The results obtained indicate a broad prospect of using the formed structures in the field of integrated optoelectronic devices.

Keywords: metal-induced catalytic growth, noble metal nanoparticle, transition metal oxides, optoelectronic device

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Влияние наночастиц благородных металлов на магнетронное распыление оксидов переходных металлов

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Аннотация. Целью данной работы является изучение особенностей формирования оксидов переходных металлов с металлическими наночастицами. Предложена технология формирования материалов, состоящая из магнетронного напыления оксидной матрицы, термокоагуляции наночастиц благородных металлов и покрытия их оксидом. В качестве исследуемых материалов использовались наночастицы золота, оксиды никеля и титана. Обнаружен металлоиндуцированный каталитический рост оксидов никеля и титана на наночастицах золота. Показано, что образующийся верхний слой имеет ярко выраженную текстуру. В процессе образуются конусы с углом раскрытия 10—12° и преимущественным направлением роста, совпадающим с кристаллографической осью, перпендикулярной поверхности (111). Исследованы оптические и электрические характеристики сформированных покрытий. Полученные результаты указывают на широкую перспективу использования сформированных структур в области интегральных оптоэлектронных устройств.

Ключевые слова: металл-индуцированный каталитический рост, наночастицы благородных металлов, оксиды переходных металлов, оптоэлектронное устройство

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Introduction

For the last decades there is a growing need for functional layers with tailored optoelectrical properties, however the bare materials does not usually provide the required characteristics [1, 2]. Thereat, a mixture of materials with precisely guided organization in order to enhance the device features is required. In this respect the noble metal nanoparticles (NPs) dispersed inside semiconductor matrices have recently been under extensive study as high-performance active layers material in numerous integrated optoelectronic devices [3]. Generally, active layers are formed in thin film configuration by using chemical deposition (wet chemistry [4] or CVD [5]), and physical (magnetron deposition [6]). The former are convenient in that they allow the matrix and a filler formation in one process, the latter are more technologically applicable. A wide range of chemical and physical techniques are also used to obtain noble metal nanoparticles [7]. However, despite each of physical techniques requiring expensive deposition equipment, they produce films with sufficient control of NP size, size distribution, and spatial distribution within the layer.

This paper is focused on the metal oxide film (MOF) deposition on AuNPs research for potential enhancement of properties for optoelectronic devices. The purpose of this work is to study the transition metal oxides with metal nanoparticles structures formation features using nickel and titanium oxides as an example and to investigate the optical and electrical properties of the formed functional coatings.

Materials and Methods

In this work, TiO_2 films were obtained by reactive magnetron sputtering (DC) with a Ti target in an O/Ar gas mixture on amorphous quartz and Si substrates. The gas ratio varied in the range 0.2–1 at an operating pressure of 1.8 mTorr. NiO films were obtained by reactive magnetron sputtering (DC) with a Ni target in an O/Ar gas mixture on amorphous quartz and Si substrates. The gas ratio varied in the range 0.2–1 at an operating pressure of 1.8 mTorr. The film's thicknesses were controlled by ellipsometry and stands at 50–100 nm. The technique described in [8] were used for AuNP formation.

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 behavior of TiO_2 and NiO on gold nanoparticles were investigated in terms of texturing and crystallinity. The technique described in [9] were used for electrical and optical experiments.

Results and Discussion

SEM images of cleavages show two oxide layers, between which there is a clearly defined boundary (Fig.1). In both cases, the formation of an oxide layer with a pronounced structure was observed above the boundary. At the boundary, there are Au nanocrystallites, the average grain size of 50 ± 1 nm.

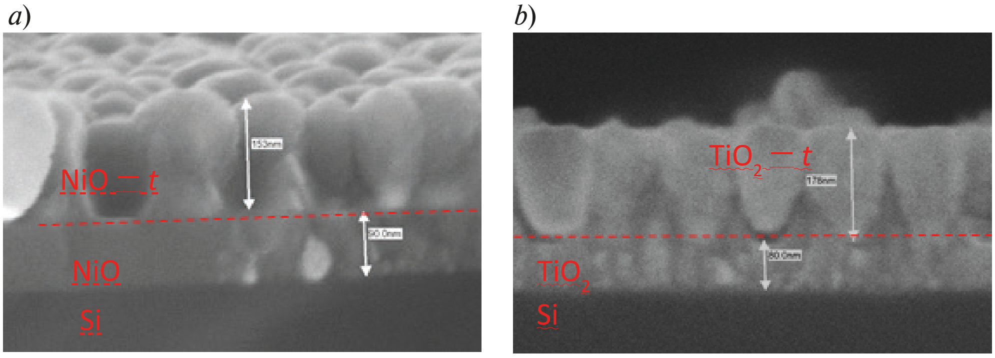

Fig. 1. Cross-sectional images of fabricated nanostructure (Si/NiO/AuNP/NiO (*a*) and Si/TiO_2/AuNP/TiO_2) (*b*)

In the case of Si/NiO/AuNP/NiO (SNAN) (Fig.2, *a*), the EDS results show the presence of O, Si, Ni and Au. In the case of SNAN, the average size of bunsenite crystallites in the lower and upper layers was 35 ± 2 nm and 45 ± 1 nm. The layers differ in the predominant orientation of crystallites (200) and (111), respectively. It was supposed that Au particles acted as a catalyst for the formation of nickel oxide textured in the (111) direction.

The EDS results for Si/TiO_2/AuNP/TiO_2 (STAT) indicate the presence of O, Si, Ti, and Au. In the case of STAT (Fig.2, *b*), the average size of anatase crystallites was 70 ± 1 nm, and for rutile, 100 ± 5 nm. That is, the presence of Au particles also contributed to the formation of texture. That is, the presence of gold nanoparticles on the oxide surface provokes the formation of a textured oxide layer.

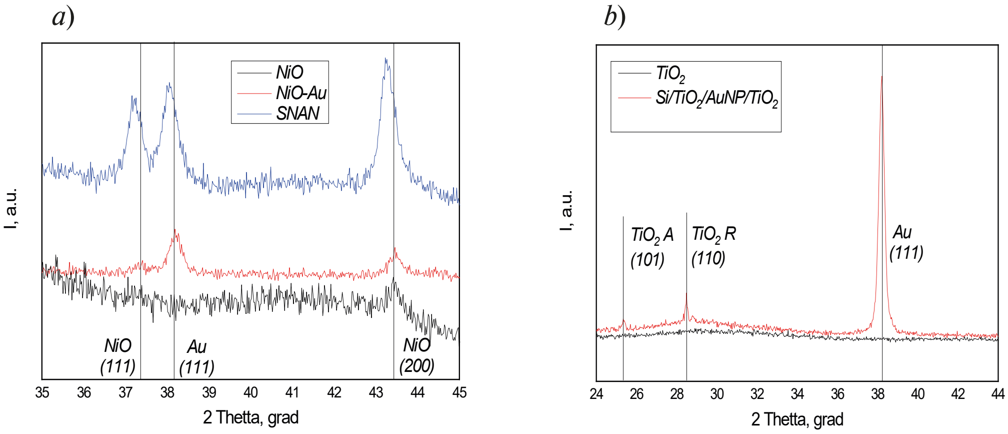

Fig. 2. XRD spectra of fabricated heterostructures

A similar behavior of systems is described for *a*-Si crystallization. It is known that a strong covalent bond is present in a bulk crystal, which is responsible for the high crystallization temperature. However, covalent bonds in *a*-Si weaken at the interface with the metal layer [10], which ensures a relatively high mobility of atoms at the interface. This fact can ensure the crystallization of *a*-Si at low temperatures. The bond weakening effect is a local electronic interaction, and the thickness of the free interfacial silicon layer is estimated at approximately 2 Si monolayers.

In immiscible metal/semiconductor systems, these two monolayers of interfacial free atoms in *a*-Si can mediate the low temperature crystallization process by (i) crystallizing at the metal interface and/or (ii) diffusing through the metal grain to the outer boundary of the system.

The ratio of the probabilities of the occurrence of these processes is determined by the ratio between the change in the "bulk" Gibbs energies and the change in the corresponding surface and interfacial energies. This process is called Metal-Induced Crystallization (MIC).

In the case of the considered oxide systems, directional crystallization is observed at the metal/semiconductor interface, which is supported by the additional introduction of material into the system during magnetron deposition of the material. During the process, cones are formed with an opening angle of 10-12° and a predominant growth direction coinciding with the crystallographic axis perpendicular to the (111) surface. A similar behavior of the deposit during magnetron sputtering was observed in the [11] for gold nanoparticles.

The formed structures showed a significant increase in the electrical response when illuminated with visible light [8], which indicates the prospects for the use of these materials as optically active layers in devices for various purposes.

Conclusion

In this work the transition metal oxides with metal nanoparticles structures formation features were demonstrated. A novel technology is proposed, consisting of the oxide layer magnetron sputtering, Au nanoparticles thermal evaporation and dewetting. Through covering it with oxide the MIC growth of nickel and titanium oxides on gold nanoparticles has been found. The optical and electrical characteristics of the formed NiO and TiO_2 based coatings were investigated. The results obtained indicate a broad prospect of using the formed structures in the field of integrated optoelectronic devices.

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