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Analysis of the optical characteristics of dendritic Ag nanostructures on c-Si by spectroscopic ellipsometry

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Dendritic silver nanostructures of different morphologies and heights from 210 to 1030 nm were obtained on the surfaces of silicon substrates using the method of chemical deposition from $AgNO_3$ + HF solution. The Bruggeman, Tauc-Lorentz, Gauss and Drude models were used to analyze optical properties, layer thickness and filling factor when interpreting experimental ellipsometric data. As a result, good convergence of the experimental and calculated spectra of the real $< \varepsilon_1 >$ and imaginary $< \varepsilon_2 >$ parts of the complex pseudo-dielectric function $< \varepsilon >$ was obtained.

Keywords: spectroscopic ellipsometry, silver dendrites, silicon.

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1. Introduction

Metal nanostructures are the object of active research due to their unique physical properties and potential applications in various fields of science and engineering. The morphology of metal structures may be complicated and highly developed, therefore the analysis of their optical characteristics is often complicated. Spectroscopic ellipsometry (SE) is a contactless non-destructive optical method, a powerful tool for studying characteristics of the rough surfaces, interfaces and thin films. Using SE, one may obtain such important characteristics of a sample as a refractive index (n), absorption coefficient (k), and one of the most important characteristics for the plasmonic structures — complex permittivity of the material (ε). Knowledge of n, k and ε coefficients of the investigated materials is critical for design of optical devices, and SE makes it possible to determine these parameters in a wide spectral range [1–4].

SE is used to investigate properties of the optically smooth surfaces or thin films [1,5]. However, in reality the investigated specimens are rarely ideally smooth, at the same time even small changes in the surface roughness may strongly impact the measured optical properties [6]. Therefore, to interpret data obtained by SE method for rough heterogeneous surfaces, multilayer structures and structures with complex morphology, various models were developed. For example, for multilayer structures the Maxwell-Garnett or Bruggeman effective medium approximations are used [2,7,8], which help to define the volume fractions (factors) of layers filling with different materials. For analysis of the experimental optical characteristics of metal nanostructures, which may not be described by tabular data of the materials they consist of, Drude, Lorentz, Gaussian, Tauc-Lorentz, Tanguy and other models are applied [2,9–14].

In this article the dendritic Ag nanostructures on silicon substrates were investigated using SE method. Such metal nanostructures are often offered as substrates with surface-enhanced Raman scattering [9,15–18]. Therefore, the study of the nanostructures presented in this work both helps to understand their optical characteristics and opens new prospects for design of optical devices with improved properties and efficiency.

2. Method of creation and morphology of dendritic Ag structures on c-Si

Boron doped (p-type) monocrystalline silicon (c-Si) with a resistivity of 10 Ω·cm and crystallographic orientation (111) was used as a substrate for creating dendritic Ag structures. During the experiment the c-Si wafers were subjected to standard cleaning, and then were placed into solution $0.02M AgNO_3 + 5M HF$ (volume ratio: 5:1) at room temperature. To create dendritic Ag structures of various morphology, the following time of substrate treatment in the solution was selected: 40 s (sample N1), 60 s (sample N2) and 90 s (sample N3). Morphology of the dendritic nanostructures was studied using a scanning-electron microscope (SEM) JSM-7001F (JEOL, Japan) in the secondary electron mode with accelerating voltage 5 kV. Fig. 1 presents SEM-images of the studied structures. The received images were used to calculate Ag layer thickness values on all substrates: 210 ± 50 nm for sample N1, 595 ± 140 nm for sample N2, 1030 ± 200 nm for sample N3.

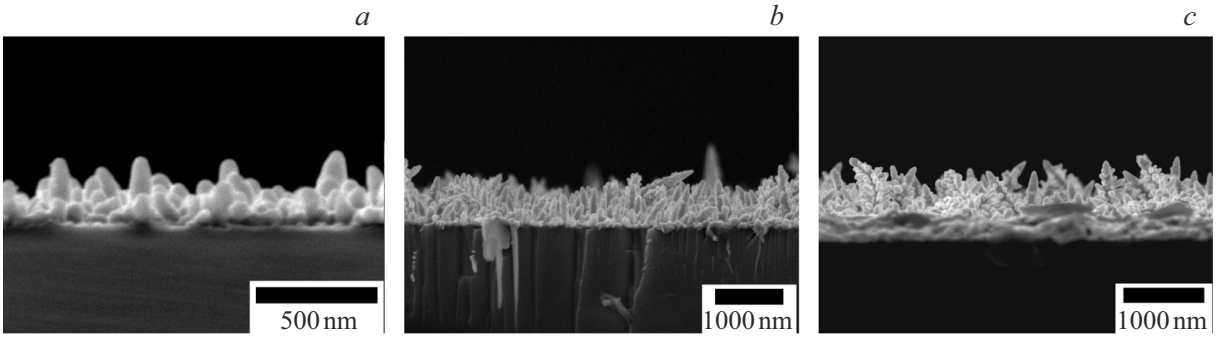

Figure 1. SEM-images of cross sections of dendritic Ag nanostructures on c-Si: (*a*) sample N1, (*b*) sample N2, (*c*) sample N3.

3. Study of optical properties by SE method

Ellipsometric properties were studied using the SE-2000 (Semilab, Hungary) spectroscopic ellipsometer in the wavelength range from 300 to 900 nm at the incident angle $\varphi = 70^\circ$. Simultaneously, two ellipsometric angles Ψ and Δ are measured, which are used to calculate the pseudodielectric function [2,9]. The measured spectra of the studied specimens are presented in fig. 2 (solid curves). To describe the experimental spectra, the dispersion models shown below are used.

Anisotropic model

Since the sample is disordered, in directions x and y the morphology may be assumed to be identical, and in direction z it differs. Therefore, the dielectric function is specified as follows: $\varepsilon_x = \varepsilon_y \neq \varepsilon_z$. Samples N2, N3 differ from N1 by height of Ag layer (more than 500 nm), as a result of which in the studied range (300−900 nm) it is not possible to see the optical response of the entire Ag/air layer. The absence of the impact from the change in the Ag/air layer thickness at the optical properties of the model of samples N2, N3 leads to the experimental spectra showing only the properties of Ag/air layer with uncertain thickness. The dielectric function of the Ag/air layer was specified by the Bruggeman effective medium approximation, in which optical properties of the silver structures were defined using the Drude, Tauc-Lorentz and Gauss models.

Drude model

This model expresses absorption of light with free electrons, where E_P and E_Γ are energies of plasma and decay, related to the scattering frequency [14]. For sample N1 parameters E_P and E_Γ were 6.9 and 0.99 eV; for N2 in plane xy E_P and E_Γ — 6.5 and 0.71 eV, respectively; for N3 in plane xy E_P and E_Γ were 7.8 and 0.71 eV.

Tauc-Lorentz model

This model displays the impact of interband transitions on the permittivity, where A is oscillator amplitude, E_0 — position, C — oscillator width and E_g — interband transition width [13]. For sample N1 a Tauc-Lorentz oscillator was used with parameters A, E_0, C and E_g, equal to 919, 3.7, 5 and 2.7 eV, respectively. For sample N2 in plane xy parameters A, E_0, C and E_g were $1.5 \cdot 10^3$, 3.7, 1.2 and 3 eV, respectively. For sample N3 in plane xy parameters A, E_0, C and E_g were $1.8 \cdot 10^3 1.8 \cdot 10^3$, 4.0, 1.1 and 3.6 eV.

Gaussian model

This model is a harmonic oscillator that describes plasmon resonances in the material. The table presents parameters approximated by Gaussian model for each sample, where F is amplitude, E_0 — position, B_r — oscillator damping [2]. As a result of approximation, the calculated (dash-dotted curves) and experimental (solid curves) spectra (Fig. 2) are in a good agreement, at the same time the determination coefficient (R^2) for N1 is equal to 0.87, for N2 — 0.95, for N3 — 0.91. Gaussian peaks at 3.9, 3.92, 3.9 eV describe „volume“ plasmon resonance of Ag, and peaks at 2.43, 1.28, 3.08, 1.5, 3.12, 1.2, 1.57 eV describe localized plasmon resonance.

Conclusion

In this paper the method of chemical Ag reduction from solution $AgNO_3 + HF$ on the c-Si surface was used to create silver dendritic nanostructures. SE method was used to characterize the produced structures in the wavelength range of 300−900 nm at the incident angle 70°. To interpret the measured ellipsometric data, Bruggeman, Tauc-Lorentz, Gaussian and Drude models were used. As a result, good convergence was obtained for the experimental spectra of the real and imaginary parts of the complex pseudodielectric function with calculated spectra, the positions of „volume“ and localized plasmon resonances of dendritic Ag nanostructures were determined. The obtained result demonstrates the possibility and the prospects of using the

Parameters of Gaussian model for samples N1, N2, N3

N1			N2			N3		
Plane xy, z			Plane xy			Plane xy		
F	E_0, eV	B_r, eV	F	E_0, eV	B_r, eV	F	E_0, eV	B_r, eV
229.9	2.43	0.28	423	1.28	0.48	10	1.2	0.36
			208	3.08	0.25			
Plane z			Plane z			Plane z		
0.05	3.9	0.09	0.04	3.92	0.08	0.09	3.9	0.04
			0.44	1.5	0.11	0.77	1.57	0.23
			0.014	3.12	1.24			

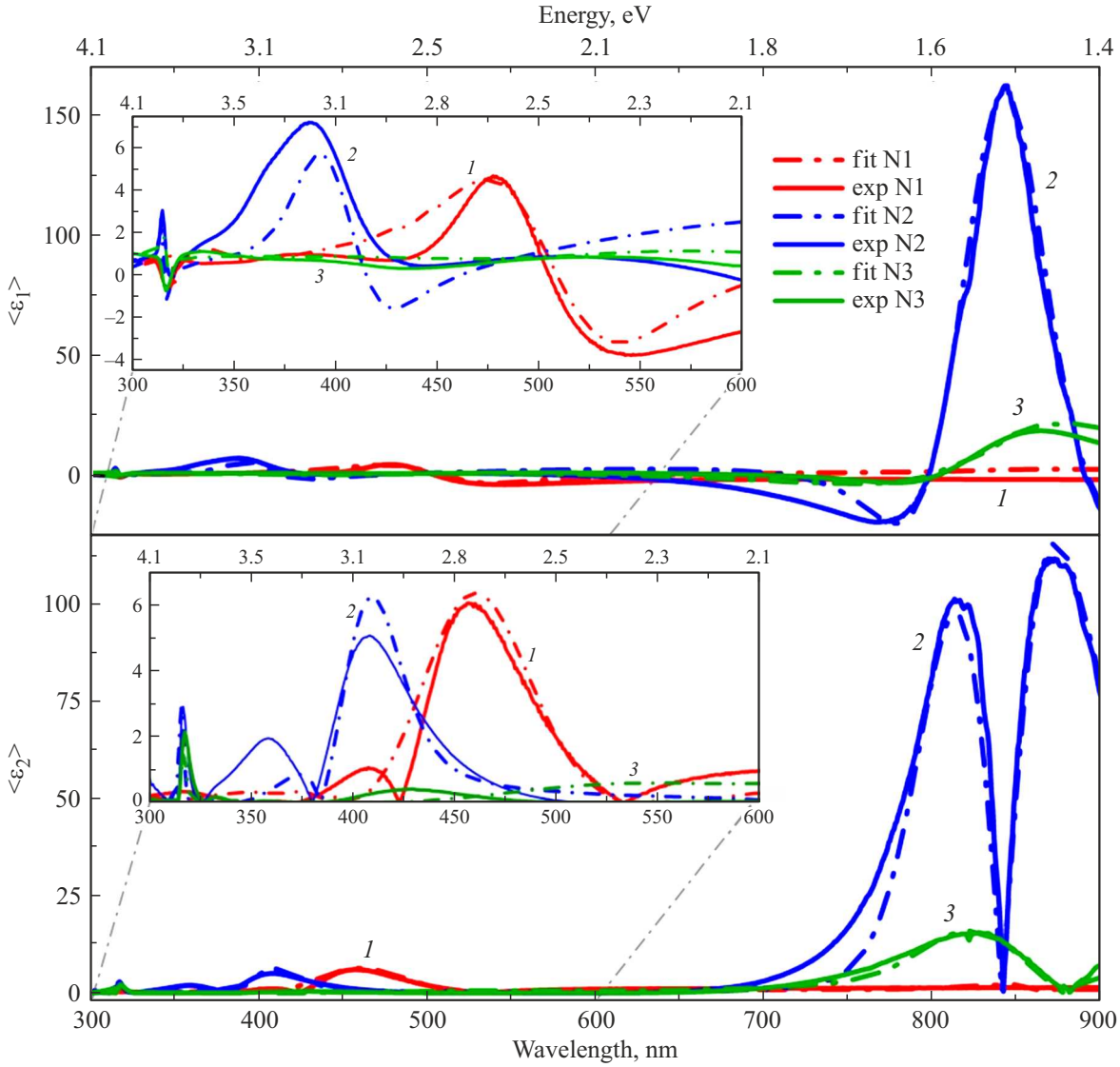

Figure 2. Measured (solid curves) by SE method and approximated (dash-dotted curves) spectra of real $< \varepsilon_1 >$ and imaginary $< \varepsilon_2 >$ parts of complex pseudo-dielectric function $< \varepsilon >$ of samples N1 (*1*), N2 (*2*), N3 (*3*), $\varphi = 70°$.

models proposed in this work to describe the optical characteristics of such complex and morphologically developed structures.

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Conflict of interest

The authors declare that they have no conflict of interest.

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