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Synthesis and characterization of titanium nitride thin films for enhancement and localization of optical fields



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ABSTRACT

Emerging plasmonic materials are an essential driving factor of the ongoing progress towards the empowering of photonic devices functionalities and performance improvement. Transition metal nitrides, being refractory metals with tunable optical properties, are prominent representatives of alternative plasmonic materials. Recent intensive examination of linear and nonlinear optical parameters of metal nitrides has revealed TiN to be a promising media for metal-based optics. Another distinctive feature of TiN is its Raman activity. In contrast to Raman-silent metals, TiN-based structures enable nonlinear light frequency conversion not only to even and odd harmonics, but also to Raman-shifted modes. Moreover, the threshold of the underlying stimulated Raman scattering (SRS) effect in these structures could be greatly reduced by appropriate geometry and material design. Here we experimentally investigate the effect of structure and composition of TiN on its optical properties, such as dielectric permittivity and third-order Raman susceptibility. A special attention is given to synthesis and characterization of TiN thin films suitable for plasmon-assisted localization and amplification of optical signals.

1. Introduction

Plasmonic excitations provide unprecedented abilities on control of electromagnetic fields and boosting light-matter interaction. Structures supporting surface plasmon polaritons (SPP) form the basis for transformation optics [1], metamaterials and metasurfaces [2,3], enhanced spectroscopies [4], nano-imaging [5], bio-sensorics [6], to name a few. Further progress towards development of innovative photonic devices is associated with nonlinear plasmonics [7,8]. This relatively new field is intended to harness the diversity of nonlinear optical effects for empowering photonic devices functionalities. However, conventional plasmonic materials are unsuitable for metal-based nonlinear optics due to low photo-induced damage threshold [9]. There is a growing demand for plasmonic media with high melting point, mechanical and chemical stability.

Recently, a new class of alternative plasmonic materials – transition metal nitrides – has been suggested to improve the performance of plasmon-assisted devices [10]. It has been demonstrated that titanium nitride (TiN) has large figure-of-merit (FOM) of plasmon resonance in visible and infra-red ranges as well as capable to withstand the light intensities required for nonlinear optical regime. These properties make

TiN attractive for applications in nonlinear plasmonics [11]. Another distinctive feature of TiN is its Raman activity. Surface plasmon wave, excited at the interface between TiN and some dielectric, experience inelastic scattering on phonons within a TiN lattice. This process leads to SPP excitation at Stokes and anti-Stokes frequencies. These localized waves can interact with each other through the third-order nonlinearity. The above effect is analogues to well-known stimulated Raman scattering (SRS) of high-intensity free-space waves in the Raman-active media [12]. The efficiency of this process can be quite large, with up to 50% of the power of the incident light being converted into one of possible Stokes waves. Thus, in contrast to Raman-silent plasmonic materials, TiN-based structures enable nonlinear light frequency conversion not only to even and odd harmonics, but also to Raman-shifted modes. Moreover, that generated signal exists in the form of localized wave because its frequency remains within plasmon excitation spectra. In order to detect the nonlinear Raman response in the far field an out-coupling of enhanced signal from the metal surface is required. Thus, TiN is the promising material from the perspective of amplification of localized optical signals.

In this work we investigate the effect of structure and composition of synthesized TiN thin films on its linear and nonlinear optical

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parameters, such as dielectric permittivity and third-order Raman susceptibility. The results of this study provide the route to fabrication of refractory TiN thin films suitable for applications in plasmon-assisted photonic devices, such as nanosized Raman lasers and ultra-sensitive bio-sensors.

2. Experimental details

2.1. TiN thin films preparation and characterization

DC reactive magnetron sputtering of Ti target (99.99% purity) in argon-nitrogen environment was employed to deposit thin films of TiN on Si(111) substrates. The purity of working (Ar) and reactive (N₂) gases was 99.9999%. As a result, a series of TiN films sputtered at different argon to nitrogen ratios (ranging from 0.625 to 50) were fabricated. The substrates were kept either at room temperature or at temperatures of 350 °C and 500 °C during deposition. The heating was accomplished through radiative heat transfer from tungsten filament. All depositions were performed within ultrahigh vacuum chamber (BESTEC, Germany). The residual pressure was $5 \cdot 10^{-7}$ Pa. The power of dc generator was fixed at 100 W. The working pressure of mixture of gases was 0.6 Pa. The silicon substrates were cleaned with isopropanol and then distilled water within ultrasonic bath. A final step of substrate preparation was Ar⁺ ion beam etching within ultrahigh vacuum chamber prior to film deposition. The energy of Ar⁺ ions was 2 keV and the ion current density was 10 mA/cm². The substrates were etched until the surface contaminations were completely removed that was confirmed by X-ray photoelectron spectroscopy (XPS).

The chemical composition of synthesized films was determined using XPS. As-deposited samples were transferred from the synthesis chamber to the analytical cell at ultrahigh vacuum conditions (base pressure $5 \cdot 10^{-7}$ Pa). XPS spectra were registered using non-monochromatic X-ray Mg-K α source and hemispherical electron energy analyzer Phoebos 150 (both from SPECS GmbH, Germany). Pass energy of 100 eV was used for survey scanning (step size 1 eV), while 20 eV pass energies were used for high-resolution measurements (step size 0.1 eV). The spectrometer was calibrated employing as a reference the Ag 3d_{5/2} peak (368.2 eV) of sputter-cleaned silver plate. XPS spectra registered from TiN samples were analyzed with the CasaXPS software (Casa Software Ltd) using Shirley-type background. The elemental concentrations of titanium, nitrogen and oxygen were retrieved from the area of the Ti 2p, N 1s and O 1s peaks, respectively. Sensitivity factors were provided by instrument manufacturer. Following the film deposition and XPS analysis TiN films were exposed to air at room temperature. The sample temperature during post-deposition venting of the vacuum chamber has a large impact on surface chemistry of TiN films [13]. Plasmonic properties of sputtered TiN thin films were analyzed via spectroscopic ellipsometry (VASE, J. A. Woolam Co., USA). The crystal structure of TiN samples was studied using Raman spectroscopy. Raman spectra were recorded using NTEGRA SPECTRA system (NT-MDT, Russia). The excitation wavelength was 632.8 nm and the light intensity in the sample plane was ~ 1 MW/cm². For measurement of nonlinear Raman characteristics the pulsed photothermal reflectance technique was applied [14]. The wavelength of the pump and probe radiation was 800 nm, and the beam flux was 12 mJ/cm². The thicknesses of TiN films were measured using stylus profilometer Dektak XT (BRUKER, Germany).

3. Results and discussion

3.1. Chemical composition

A series of TiN thin films were sputter-deposited at different Ar/N₂ ratios and substrate temperatures within ultrahigh vacuum chamber. The main synthesis parameters are presented in Table 1. The chemical composition of TiN films, sputtered under different conditions as given

in Table 1, was determined via XPS. The XPS measurements were carried out in ultrahigh vacuum chamber without contact of the samples with air as well as after exposure to air. As can be seen from Table 1, as-deposited samples exhibit rather high content of oxygen despite the fact that the base vacuum was ultrahigh ($5 \cdot 10^{-7}$ Pa). Moreover, TiN films were fabricated using ultrapure gases (Ar and N₂) with purity of 99.9999%. Therefore, the presence of the oxygen in the as-deposited TiN was attributed to degassing of the gas line. Further increase in oxygen concentration for samples exposed to air is caused by oxidation of the film surface. Fig. 1 shows XPS core level spectra obtained from the TiN (sample 7) and a pure Ti layer. As follows from XPS data, Ti 2p spectrum of TiN has a complicated structure. The spectrum exhibits intense peaks located at the binding energies indicative for TiN formation [15,16]. In order to establish the formation of TiO_xN_y and TiO₂ phases as well as to estimate their relative percentage the deconvolution of XPS spectrum is required. The approach for unambiguous XPS spectra deconvolution based on cross-peak self-consistency can be found in Ref. [17].

3.2. Linear optical properties

Plasmonic properties of sputtered TiN thin films were analyzed via spectroscopic ellipsometry. Fig. 2 shows real and imaginary parts of dielectric function of TiN with different structure and composition. We observed the similar dependence of dielectric permittivity on nitrogen concentration in TiN samples, as reported in [18]. The increase of nitrogen content results in growth of the charge carrier's concentration, which in turn leads to decrease of the Re[ϵ] magnitude. As seen from the Fig. 2, all prepared films can potentially be plasmonic (Re[ϵ] < 0) for wavelength above 480 nm, although the ohmic losses are still high compared to gold (blue curve) in visible and infrared ranges [19]. In visible range, the finest plasmonic properties (according to Frohlich conditions) attained in our experiments correspond to sample 2 (pink curve).

3.3. Raman spectroscopy

TiN has cubic face centred crystal structure with O_h symmetry, thus first-order Raman scattering is forbidden by selection rules [20]. However, according to Fig. 3, the first-order peaks at 240 cm⁻¹ (TA), 310 cm⁻¹ (LA) and 560 cm⁻¹ (TO) were observed. This is caused by high concentration of defects within film leading to local symmetry breaking. It is important to note the considerable increase of spectra intensity in the 100–300 cm⁻¹ range for films deposited on heated substrates. This is due to the growing number of vacancies in both sublattices (Ti and N). The peak at 620 cm⁻¹ (LO) corresponds to Ti atoms surrounded by nitrogen vacancies and N atoms surrounded by titanium vacancies. The peaks at 440 cm⁻¹ (2TA) and 820 cm⁻¹ (TA + LO) originating from two-phonon scattering are not observed for samples prepared on heated substrates. This is caused by increase of the nitrogen vacancies, which is further confirmed by growth of acoustic bands. Importantly, the high level of vacancies concentration within TiN may occur even in the films with stoichiometric structure.

The efficiency of SRS process is described via third-order Raman susceptibility, which is given by [12].

$$\chi_R^{(3)} = \epsilon_0 \frac{N}{m} \left(\frac{\partial \alpha}{\partial q} \right)_0^2 \frac{1}{\omega_v^2 - \Omega^2 + 2i\gamma\Omega} \quad (1)$$

Here, ϵ_0 is the vacuum permittivity, N stands for a number of scattering molecules, m represents the reduced nuclear mass, $(\partial \alpha / \partial q)_0$ is a Raman polarizability, $\Omega = \omega - \omega_s$ denotes the difference between initial and Stokes frequencies, ω_v and γ is the resonance frequency and damping constant of molecular vibration respectively. The Raman resonance condition $\Omega = \omega_v$ is automatically fulfilled when the wave propagates in the Raman-active media. For measurement of the

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