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Plasmonic properties of titanium nitride thin films prepared by ion beam assisted deposition

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ABSTRACT

Titanium nitride (TiN_x) is regarded as a kind of promising plasmonic material for its high performances. We studied the influence of nitrogen partial pressure p_n and deposition temperature T_d on the structural and plasmonic properties of the TiN_x thin films prepared by ion beam assisted deposition (IBAD). The results show that IBAD is an effective method to tailor the plasmonic properties of TiN_x films in visible and near-IR region. The plasmonic properties of the films have significant T_d and p_n dependence. Higher p_n and lower T_d can reduce the plasma frequency and the plasmon resonance. Higher p_n and higher T_d can reduce the optical loss of the samples. The modification of the plasmonic properties is related to the variation of nitrogen content.

1. Introduction

The research for the high-density integration of optical and electrical devices for compact photonics transducers and ultrasensitive chemical sensors has significantly driven the recent advancements of plasmonics and metamaterials technologies [1–3]. Initially, only gold and silver were used as plasmonic materials [4]. However, their excessive losses at visible optical and near-infrared spectral range, and limited tunability, severely constrain their practical implementations [4,5].

In recent years, transition-metal nitrides, such as titanium nitride (TiN_x), have emerged as alternative plasmonic materials in the visible and near-infrared spectral range [5,6]. TiN features outstanding CMOS compatibility, refractory properties, chemical and mechanical stability [7–9], and has been used in many devices such as single photon sources [10], perfect absorbers [8], emitter [11], and nanoantenna arrays [12]. As a kind of non-stoichiometric material, its plasmonic properties can be tuned by experimental parameters in preparation [5,13].

Most of the TiN_x samples in the research of its plasmonic properties were fabricated by magnetron sputtering [13] and atomic layer deposition [12]. In this work, we prepared TiN_x films by ion beam assisted deposition (IBAD). Ion beam modification has been used in many fields, while rarely in the research of plasmonics. We also have studied IBAD-TiN_x films, but the efforts were focused on the orientation and morphology [14]. Many properties of the IBAD films can be tailored by manufacture process conditions. Especially, the implantation of nitrogen ions can tune the stoichiometry (x value) of the TiN_x films. In this work, we tuned the nitrogen content N% by nitrogen partial pressure p_n. The influence of p_n and deposition temperature T_d on the structural and plasmonic properties were investigated. Our results show that IBAD-TiN_x can be used as a kind of plasmonic material in visible and near-IR region, and its plasmonic properties can be effectively tuned by p_n and T_d.

2. Experimental details

An IBAD system with two Kaufman ion sources was employed to prepare IBAD-TiN_x thin films. One (ϕ8 cm) served as a sputtering source and the other (ϕ6 cm) as an assisting source. Deposition atoms were sputtered by a sputtering Ar^+ beam from a 99.99% pure TiN_x target and deposited on $10 \times 10\ mm^2$ sized glass substrates for an hour. The sputtering ion beam energy and current were kept constant at 800 eV and 90 mA. The base pressure was about 4×10^{-4} Pa, and the working pressure was about 3×10^{-2} Pa. The growing films were bombarded by an assisting beam mixed with argon and nitrogen ions. The incident angle of

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assisting ion beam was 45°. N_2 partial pressure p_n was changed by the flow rate ratio of N_2 to Ar. p_n and deposition temperature T_d varied while assisting ion beam energy and current were kept invariant at 200 eV and 10 mA. All the films are 150($\pm$10) nm thick, which was obtained by a surface profile system (Veeco Dektak150).

3. Results and discussion

Fig. 1 (a) shows the X-ray diffraction (XRD) patterns of all the samples, which were got by XRD system (D/MAX-RB) equipped with Cu-Kα1 source. Only obvious (111) peaks appear, which reflects that a (111)-oriented face-centered cubic structure formed. The XRD ϕ-scan results show no in-plane preferred orientation appears in all the films. Thus we can say a polycrystalline structure with preferred (111)-orientation was formed. The intensity of (111) peak becomes weaker with p_n rising, which can be attributed to the increasing number of interstitial defects. The nitride content $N\%$ values were measured by an energy dispersive spectrometer system, and indicated on the corresponding curves. All the films are overstoichiometric, and the higher p_n leads to more interstitial N atoms and inhabits the crystallinity. Higher T_d raises the evaporation of N atoms and reduces the N%, so the crystallinity was enhanced at 400 °C. The intensity of (111) peak at 600 °C is depressed, because too high T_d causes more Frenkel defects.

Fig. 1(b) and (c) exhibit the real part ε' of the permittivity with different p_n and different T_d. ε' was obtained by

$$\varepsilon' = n_0^2 - \kappa^2 \tag{1}$$

where, n_0 and κ are refractive index and extinction coefficient respectively, the measurement of which was performed using a spectroscopic ellipsometer (Smart SE). Fig. 1(b) tells that TiN_x thin films are dielectric in short wavelength, but turn metallic in long wavelength. The dielectric and metallic properties of TiN_x are associated with intraband and interband absorption respectively [13]. The cross-over frequency ω_c, namely screened plasmon frequency, defined as the frequency at which the real permittivity of the material crosses zero, decreases with p_n rising, while increases with T_d rising. Since ω_c is directly proportional to plasma frequency ω_p, and ω_p is proportional to the square of carrier concentration [5,13], the result proves that lower carrier concentration is caused by higher p_n, while higher T_d results in higher carrier concentration. Importantly, the carrier concentration and plasma frequency of TiN_x thin films can be effectively tuned by p_n and T_d.

In Fig. 1(b) and (c), the intersection $\varepsilon' = 0$ with a positive slope at $E_p{}'$ of different values indicates a longitudinal excitation mode, namely the screened plasmon mode. $E_p{}'$ defined by the energy at which $\varepsilon'=0$, can be used to monitor the composition and stoichiometry of TiN_x. It has been reported that $E_p{}' = 2.6$ eV for $TiN_x(x = 1.0)$ and $E_p{}' < 2.6$ eV for overstoichiometric $TiN_x(x > 1.0)$ [15,16]. Thus we can consider that the TiN_x films become more and more overstoichiometric with p_n increasing in Fig. 1(b). While, the films become more and more stoichiometric with T_d rising, as evidenced in Fig. 1(c). Above results rightly conform with the N% law in Fig. 1(a). The dependence of ω_c and carrier concentration n on p_n and T_d discussed above is caused by different N%.

Fig. 2 visualizes the effect of p_n and T_d on the spectra dependence of the imaginary part ε'' of the permittivity. ε'' was obtained by

$$\varepsilon'' = 2n_0\kappa \tag{2}$$

We can observe that with the wavelength ranging from the visible to near-IR region, ε'' values for all the films augment and become more and more obvious.

ε'' reflects the optical losses of the samples. In Fig. 2, the losses are not small, compared to that of noble metal [4], partly because of the presence of interband transition losses. In the regions where interband losses are absent, the losses are mainly due to Drude damping [13]. However, the losses of TiN_x thin films can be reduced by p_n and T_d. The insets in Fig. 2 illustrate the ε'' value ε''_c at screened plasma wavelength λ_c, which is defined as the wavelength meeting $\varepsilon'=0$. The results also indicate that ε''_c can be reduced by lower p_n and higher T_d.

We can compare the loss calculated from optical data with the energy loss spectrum of fast electrons traversing a crystalline material. The energy-loss function [16]:

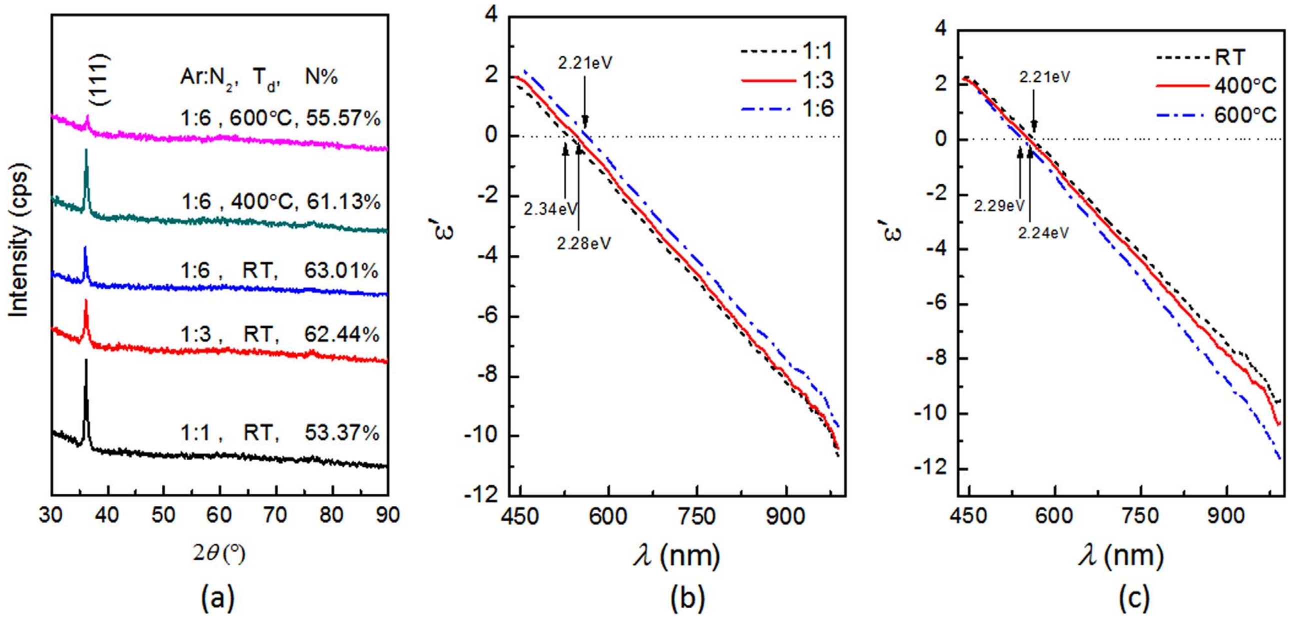

Fig. 1. XRD patterns and real part ε' of the permittivity of the TiN_x thin films. (a) XRD results, The nitride content $N\%$ values are indicated; (b) and (c): ε' of the permittivity of the films prepared with different p_n (b) and T_d (c). The vertical arrows illustrate the screened plasmon energy.