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Evolution of optical properties with deposition time of silicon nitride and diamond-like carbon films deposited by radio-frequency plasma-enhanced chemical vapor deposition method

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ABSTRACT

The paper presents investigations of the optical properties of thin high-refractive-index silicon nitride (SiN_x) and diamond-like carbon (DLC) films deposited by the radio-frequency plasma-enhanced chemical vapor deposition method for applications in tuning the functional properties of optical devices working in the infrared spectral range, e.g., optical sensors, filters or resonators. The deposition technique offers the ability to control the film's optical properties and thickness on the nanometer scale. We obtained thin, high-refractive-index films of both types at deposition temperatures below 350 °C, which is acceptable under the thermal budget of most optical devices. In the case of SiN_x films, it was found that for short deposition processes (up to 5 min long) the refractive index of the film increases in parallel with its thickness (up to 50 nm), while for longer processes the refractive index becomes almost constant. For DLC films, the effect of refractive index increase was observed up to 220 nm in film thickness.

1. Introduction

Plasma-deposited silicon nitride (SiN_x) and diamond-like carbon (DLC) thin films already enjoy wide application in both electronic and optical systems [1-4]. These amorphous films exhibit good (DLC) or excellent (SiN_x) adhesion to Si and SiO_2, which makes them suitable materials for silicon-based devices. In complementary metal-oxide semiconductor technology, the films typically play the role of a thin gate dielectric (usually less than 100 nm in thickness) for field-effect transistors including ion-sensitive field-effect transistors, or in their thicker form (typically 750 nm) are often employed as a passivation layer for a variety of integrated devices [2,5,6]. For both passivation and gate dielectric purposes, the films provide a good (SiN_x) or excellent (DLC) diffusion barrier against water molecules and sodium ions, two major sources of corrosion and instability in microelectronics [7,8]. Moreover, both materials exhibit very good chemical stability and inertness, qualities which are important in the design of reliable biochemical and biomedical devices. Together with high chemical stability, silicon nitride films show high values for hardness (~19 GPa) and for Young's modulus (~150 GPa), values that are respectively 2–5 and 3 times higher than those of SiO_2[9]. For their part, DLC films are considered one of the best wear-resistant materials, exhibiting hardness of over 20 GPa [10]. Due to good mechanical properties, both films are often used as a masking layer during the fabrication of integrated devices [11,12]. The combination of high hardness and high refractive index allows for application of these thin films (ranging in thickness from 50 to 200 nm, depending on their refractive index [13]) as an optimum, single-layer antireflecting and protective coating for silicon solar cells [5,14,15].

In addition to their use in microelectronics, silicon nitride and diamond-like carbon films have been applied in the fabrication of various types of optical waveguides and planar optical systems [10,16-18]. For all of the optical applications, the thickness and optical properties of the films play a critical role in ensuring the proper functioning of the device. The SiN_x films have a high refractive index in the infrared spectral range, which can be adjusted from that of Si_3N_4 ($n = 2$) to that of amorphous silicon ($n = 3.5$). In the case of DLC films, the refractive index varies with the hydrogen content and the sp^2/sp^3 ratio, exhibiting values from 1.8 to 2.2 in the infrared spectral range. Moreover, both films show very low optical absorption in the infrared and in the case of SiN_x in the visible spectral range as well. Due to these excellent optical properties, waveguides based on the films have transmission losses as low as 0.1 and 0.3 dB/cm for SiN_x and DLC films respectively [16,17]. The thickness for this type of application may be as much as 200 nm. A free-standing silicon nitride

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membrane of the same thickness has also been considered as a substrate in the design of photonic devices [7,19].

Recently some modern applications have been presented involving thin SiN_x and DLC films. The nanocoating significantly modifies the conditions of propagation for guided modes. Thus Park et al. [11] have shown that thin silicon nitride film measuring in the tens of nanometers can adjust the resonance wavelength of ring resonators. Furthermore, the sensitivity of optical fiber sensors within a specified range of the external refractive index can be precisely adjusted by appropriate choice of the thickness and optical properties of the coatings [20-22]. In previous articles, we have reported sensitivity tuning of optical fiber sensors using thin DLC films [23,24]. It can be concluded that for these applications in an ideal case, the coating should maintain its optical properties regardless of its thickness.

Deposition of SiN_x and DLC films can be achieved using one of the well established for standard silicon-integrated-circuit plasma-enhanced chemical vapor deposition (PECVD) methods. These methods offer the possibility of low-cost fabrication and high efficiency. The growth of the film is due to activation of the gas-phase precursors in a glow-discharge (plasma) environment. The chemical reactions activated by the plasma take place over the substrate as well as at the substrate. Using the PECVD system, one can deposit uniform films even on three-dimensional objects [24,25]. The materials can also be deposited as graded-refractive-index films or as a stack of nanofilms each with different properties. PECVD methods currently used include Low Pressure (LP), Radio Frequency (RF, f = 13.56 MHz) and Low Frequency (LF, f = 380 kHz) PECVD. The RF and LF PECVD methods are more attractive as processes for fabricating optical devices because they operate at lower temperatures (200 °C to 400 °C) than LP PECVD which requires temperatures in the 700° to 800 °C range [26].

In this work, we focused on investigations of SiN_x and DLC thin films deposited by RF PECVD for application in tuning the functional properties of optical devices such as optical sensors, filters and resonators. Both films showed very attractive properties from the point of view of optical applications. Our aim was to achieve thin (<100 nm), high-refractive-index SiN_x films at a substrate temperature below 350 °C, which is acceptable for the thermal budget of most of optical devices. Moreover we deposited a series of slightly thicker (up to 350 nm), high-refractive-index DLC films, where substrate temperature was significantly lower (20 °C).

2. Experimental details

The films were prepared using different plasma setups working at f = 13.56 MHz. Since for most of the applications of silicon nitride films SiO_2 or oxidized Si substrates are used, the films were deposited on oxidized p-type <111> silicon wafers (ρ = 0.005–0.02 Ω cm) using Plasmalab 80+ (Oxford Plasma Technology) [5]. We employed a high $[SiH_4{:}N_2]/[NH_3]$ flow ratio (2% SiH_4 diluted in N_2) in order to obtain high-refractive-index SiN_x films. DLC films, on the other hand, were deposited on oxidized p-type <100> silicon wafers (ρ = 6–8 Ω cm) using a home-made RF plasma system [27] equipped with a water-cooled electrode. In the setup, instead of setting RF power, we monitored negative self-bias voltage, which is a characteristic parameter of RF PECVD. We used methane (CH_4) as a carbon film gas precursor. The deposition parameters of the DLC films were optimized in terms of adhesion of the films to oxidized-silicon substrate. The deposition parameters for both types of films are given in Table 1.

Before plasma deposition and oxidation, all samples were cleaned according to the common practice in microelectronics RCA procedures. The wet oxidation process was performed in a furnace heated to 1000 °C. The oxidized wafers were then cooled down and used directly for deposition of both types of films.

Film parameters such as the index of refraction (n), the extinction coefficient (k) and the thickness were determined by a Horiba Jobin-Yvon UVISEL spectroscopic ellipsometer operating in the wavelength range from 250 nm to 2050 nm with the increment of 20 nm. The equipment was calibrated before each measurement. To fit the measurement data to a physical model, a structure containing a first SiO_2 layer covering the silicon substrate and a second SiN_x or DLC layer was applied and fitted with $\chi^2 < 1$. The SiN_x and DLC films were modeled using the single-layer Tauc–Lorentz dispersion formula [13]. In order to minimize error coming from precision of angle of incidence, which was initially set to 70°, the angle of incidence in addition to the other parameters was determined using the fitting procedure. Thickness of the SiO_2 film after the oxidation process was determined to be in range of 385 nm to 400 nm, and confirmed to be in the same range after the deposition.

Table 1
Parameters of SiN_x and DLC films deposition by the RF PECVD method.

	SiN_x	DLC
RF Power [W]	15	
Negative self-bias voltage [V]		500
Gas precursors	$(SiH_4{:}N_2)/(NH_3)$	CH_4
Gas flow [ml/min]	285/15	50
Pressure [Pa]	53	70
Deposition time [min]	1 to 10	1 to 7
Substrate temperature [°C]	300 to 340	20

3. Results and discussion

3.1. Silicon nitride films

As can be seen from Fig. 1, the optical properties of SiN_x films depend on both temperature and deposition time. The influence of substrate temperature on the refractive index of the films is greater when films are deposited in processes of shorter duration (Fig. 1a). The obtained films show significant absorption in the UV spectral range, which increases with deposition time (Fig. 1b). For films with shorter deposition times, the extinction coefficient has higher values in the visible spectral range. However, in the infrared range the extinction coefficient is negligible for all the measured films.

The dependence between the refractive index (measured at λ = 1560 nm) and the substrate temperature for different deposition times is shown in Fig. 2. Increases in temperature clearly correspond with increases in the refractive index. However, even when the substrate temperature is at the higher end of the investigated temperature range, e.g., 335 °C for the 1 min-long process, the refractive index is still highly dependent on the duration of the deposition procedure. The temperature increase cannot compensate for that effect. It can be clearly seen in Fig. 3, that the refractive index increase with film thickness up to 50 nm is approximately $5 \cdot 10^{-3}$ refractive index unit per nm (RIU/nm). For greater film thickness, the refractive index can be assumed to be deposition-time-independent and reaches 2.4 (at λ = 1560 nm). Fig. 3 also shows that the SiN_x films were deposited at a rate of 9.25 nm/min, which is low enough for good control of thickness of the films for optical applications. In contrast to the influence on optical properties, it can be seen that substrate temperature in the investigated range has very little effect on the thickness of the films.

It was shown by number of authors that the optical properties of plasma-deposited SiN_x films can be adjusted over a wide range by varying the process parameters. Typically, an increase in the refractive index can be achieved by increasing the SiH_4/NH_3 flow ratio [13,28]. Increasing the flow ratio will also reduce film roughness [28], which is beneficial from the perspective of optical applications. Moreover, it is possible to increase the pressure in the plasma chamber (up to 100 Pa), resulting in an increase of both the refractive index and the deposition rate [28].

In our experiment, we altered just two factors, substrate temperature and deposition time. The influence of substrate temperature on