Interference coatings based on synthesized silicon nitride

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Silicon nitrides are synthesized by ion-assisted deposition with only one coating material and a nitrogen-ion-beam source. All the SiN_x films are amorphous and mechanically strong. A wide range of refractive indices from 3.43 to 1.72 at a wavelength of 1550 nm is obtained. Near-IR antireflection coating and a bandpass filter based on the multilayers of SiN_x and Si are demonstrated. © 1999 Optical Society of America

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1. Introduction

SiN_x films are chemically stable and have good mechanical and optical properties. They have been synthesized by various methods and investigated by several authors.¹⁻⁹ Among those methods, either a plasma-enhanced technique or chemical vapor deposition or a combination of these techniques has been studied. Most of those studies focused on the deposition technique and the analysis of film properties. However, simplifying the deposition process and reducing the absorption loss in making optical interference coatings still remain a challenge, especially for multilayer coatings in the near-IR region.

In this paper we report the systematical studies of the synthesis of SiN_x films by electron-beam evaporation of pure Si accompanied by N-ion bombardment. This simplifies the coating process since only one coating material is needed. The results of the investigation on the composition, microhardness, and optical properties are described in detail. The optimum condition for depositing low-extinction-coefficient films is explored. The application of the fabrication of a near-IR interference coating is demonstrated.

2. Experiments

Deposition is carried out on a cryopumped chamber with a basic pressure of 7×10^{-7} Torr. Si with 99.99% purity is the only material used as the start-

ing material, and it is evaporated by an electron-beam gun. BK-7 glass and a Si wafer are used as substrates. The deposition rate r is ~ 0.07 nm/s, as measured by a quartz-crystal thickness monitor. Ion-assisted deposition is applied during the deposition. N_2 is the only gas fed into the ion source as a working gas. No other gas or N_2 is fed into the coating chamber during the synthesis of SiN_x . Figure 1 is the schematic diagram of the deposition system. The ion source is a Kaufman type made by Ion Tech Inc. Ion-beam voltage V_b and ion-beam current density J are the only two adjustable parameters for synthesizing various SiN_x . J is measured by a Faraday cup that is set beneath the substrate before each deposition.

An x-ray diffractometer, x-ray photoelectron spectroscopy (XPS), and an IR spectrophotometer are used to investigate the structure and the stoichiometry of the deposited films. A microhardness tester is used to measure the relative hardness of the coatings, which is expressed in Vickers hardness (HV).

A Hitachi Model U-3501 spectrophotometer is used to measure spectra of the synthesized films. From the spectra, the refractive indices and the extinction coefficients are calculated by the envelope method.¹⁰

3. Results and Discussions

All the SiN_x films are amorphous, as measured by the x-ray diffractometer.

The composition of SiN_x films can be found from XPS. For $J = 0$ $\mu\text{A}/\text{cm}^2$ and $J = 40$ $\mu\text{A}/\text{cm}^2$, the XPS spectra show only one peak at -99.43 eV (Fig. 2) and -102.02 eV (Fig. 3), respectively, which correspond to Si and Si_3N_4 , respectively. Figure 4 is the XPS spectrum of a SiN_x film deposited with $J = 30$ $\mu\text{A}/\text{cm}^2$. The two peaks in Fig. 4 indicate that the film could be a mixture of SiN_x with a different ratio of Si_3N_4 and Si.

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Fig. 1. Schematic diagram of the synthesis of SiN_x by IAD. PBN, plasma beam neutralizer.

No hydrogen was found, as some of the films were synthesized by chemical vapor deposition. This is also verified by examination of the absorption band in the IR spectrum. There is an absorption band only around 900 cm^{-1} that corresponds to the Si—N bond.

The synthesized SiN_x films are very hard. Table 1 shows the microhardness of the films deposited on a Si wafer and BK-7 glass. The physical thickness of the films is $\sim 300\text{ nm}$. For comparison, the microhardnesses of the Si wafer and BK-7 glass are listed in Table 1: 1070 and 652 HV, respectively. The microhardness of the Si film increases from 684 and 435 HV up to 965 and 634 HV on the Si wafer and BK-7 glass, respectively, if the deposition is assisted by Ar-ion bombardment. All the synthesis films and

Fig. 2. XPS spectrum of a Si film; $J = 0$.

Fig. 3. XPS spectrum of Si_3N_4 film, $J = 40\text{ }\mu\text{A}/\text{cm}^2$.

the Ar-ion-assisted-deposited pure Si film were abraded 20 strokes with cheesecloth and no scratches were seen with a $150\times$ microscope.

The spectra of single-layer SiN_x film deposited on BK-7 glass at various J and $V_b = 550\text{ V}$ are shown in Fig. 5. The refractive index n and the extinction coefficient k versus J at a wavelength of 1550 nm , as calculated by the envelope method,¹⁰ are shown in Fig. 6. Indices range from 1.72 to 3.43, depending on the value of J . A graded refractive-index profile is useful for fabricating rugate filters.^{11,12} The var-

Fig. 4. XPS spectrum of a SiN_x film; $J = 30\text{ }\mu\text{A}/\text{cm}^2$.

Table 1. Microhardness of Synthesized SiN_x and Si Films as a Function of Ion-Beam Current at Ion-Beam Voltage 550 V

Nitrogen-ion current density ($\mu\text{A}/\text{cm}^2$)	Substrate (Si Wafer) (HV)	Substrate (BK-7 Glass) (HV)
40	1256	747
30	1246	738
20	1148	707
10	1121	692
0	684	435
0	965	634

(But IAD with
Ar-ion beam
 $40\text{ }\mu\text{A}/\text{cm}^2$)

Hardness of Si wafer = 1070 HV

Hardness of BK-7 glass = 652 HV

Fig. 5. Spectra of SiN_x films deposited on BK-7 glass with various ion-beam current densities (J).

ious indices also benefit the fabrication of other types of optical interference coatings, as shown below.

Both n and k are V_b dependent and are optimal at 550 V. We have tried V_b from 0 to 700 V and find that the value of k increases when V_b is greater than or less than 550 V. For V_b greater than 550 V the nitrogen gases could penetrate into the film and be trapped inside the film. On the other hand, if V_b is less than 550 V, the film would not be so dense. In both cases, the film could have larger k or lower n . Such a result is consistent with the results of Ref. 13. Therefore we fixed $V_b = 550$ V and adjusted the J value to get the desired refractive indices to fabricate multilayer interference filters. Under this condition and with $J = 40 \mu\text{A}/\text{cm}^2$, we have a Si_3N_4 film with $n = 1.72$ and k less than 10^{-5} at a wavelength of 1550 nm within the experimental uncertainty of the measured transmittance.

If we assume that the synthesized SiN_x is a film composed of Si and Si_3N_4 , then the effective refractive index of the films can be derived. Let n_A and n_B be the refractive indices of two composite materials and q be the volume fraction of material A; then the effective refractive index of the composite film n , by the Bruggeman expression,^{14,15} is

$$q \frac{n_A^2 - n^2}{n_A^2 + 2n^2} + (1 - q) \frac{n_B^2 - n^2}{n_B^2 + 2n^2} = 0. \quad (1)$$

Fig. 6. Refractive index and extinction coefficient of SiN_x films at 1550 nm.

Fig. 7. Refractive index of synthesized SiN_x films versus Si_3N_4 volume fraction ($q\%$).

Let Si_3N_4 be material A; the refractive indices of the synthesized film are dependent on the fraction q , as shown in Fig. 7 (solid curve). The experimental data are quite close to the Bruggeman expression with small deviations at $q = 0.36$ and $q = 0.66$, which correspond to $J = 10 \mu\text{A}/\text{cm}^2$ and $J = 20 \mu\text{A}/\text{cm}^2$, respectively. This deviation might be due to the error in calculating the refractive index since the film is not very thick. The thickness of the film is ~ 300 nm; the peaks and valleys are therefore not very clear in the spectrum around the near-IR. This is the disadvantage of using the envelope method to calculate the refractive index if the film thickness is too thin. In any case, the curve shows that the index of the synthesized film depends on the value of q with $n = 3.43$ when $q = 0$ and $n = 1.72$ when $q = 1$ at a wavelength of 1550 nm.

From the deposition rates r and the ion-beam current density J we also find that q is a function of J and ion/atom ratio α . The relations between J versus q and α versus q are shown in Fig. 8 according to experimental data and the following equation:

$$\alpha = (J/Q)/(pr), \quad (2)$$

where $Q = 1.6 \times 10^{-19}$ C is the electron charge and $\rho = 4.9 \times 10^{22}$ atoms/ cm^3 is the atomic density for an amorphous Si.¹⁶

When $J = 40 \mu\text{A}/\text{cm}^2$ and $q = 1$, that means Si was fully nitrified. The N ion to Si atom ratio is 0.73 at that condition.

The wide range of various refractive indices of SiN_x is very useful for optical coatings. Figure 9 is an example of an antireflection (AR) coating on one side of a ground Si wafer. It is a single-layer quarter-wave SiN_x with $n = 1.85$.

Figure 10 is a short-wavelength-pass filter deposited on a Si wafer: ARC/Si-sub/M(HL)³H0.5L/Air, where M, H, and L are quarter-wave optical thickness of SiN_x with indices 2.4, 3.4, and 1.72, respectively; M is a match layer to increase the transmittance in the pass range; and ARC is an AR coating on the backside of the silicon wafer (Si-sub). The short-wavelength cut is due to the intrinsic absorption of Si. The final optical performance of the coatings is then a bandpass filter.

The above demonstration was done in a small

Fig. 8. Volume fraction ($q\%$) of Si_3N_4 versus (a) ion current density, (b) (N ion)/(Si atom) ratio.

coater. With a large crucible we then could have enough material to manufacture block filters and bandpass filters for a wavelength division multiplexer¹⁷ with only one coating material, Si, and using less layers than conventional methods. It could simplify the coating process a lot. However, reducing the k value for SiN_x , where x is less than 1.33, is necessary if a low-loss coating is required. It needs more work, such as adjusting the coating parameters and the substrate temperature and using a second ion source.

In conclusion, we have demonstrated the advantage of using an ion source in the coating process, the technique of synthesized silicon nitrides and the coating of thin-film filters, by using only one coating ma-

Fig. 9. Single-layer AR coating on one side of a ground Si wafer.

Fig. 10. Short-wavelength-pass filter deposited on a Si wafer with an AR coating on the backside.

terial. The film is mechanically strong. The coating process is much simpler and more reproducible than conventional methods.

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