Fabrication and performances of double-sided HfO$_2$ anti-reflection films with ultra-high infrared transmittance

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**Abstract**

Si is one of the most important infrared optical materials. However, the high refraction index of Si in the infrared regions leads to large reflection losses, so increasing the infrared transmittance is of great significance to practical application. HfO$_2$ film is widely investigated due to the high-k gate dielectric properties. It also has excellent optical properties to be used as anti-reflection film for Si. In this study, double-sided HfO$_2$ films (HfO$_2$/Si/HfO$_2$) were fabricated as anti-reflection coating on Si substrate to further enhance the infrared transmittance (99%). The transmittance peak can be regulated by adjusting the thickness of HfO$_2$ films. Besides, the deposition temperature had been optimized by using XRD, XPS, SEM, AFM, and optical measurements. The results indicate good crystalinity and flat surface for the samples. Furthermore, HfO$_2$ films show surface hydrophobic properties, which can prevent water in the infrared application. These encouraging results show the HfO$_2$ films have excellent application prospective for the infrared optical systems.

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1. Introduction

Infrared (IR) transparent materials play an important role in the fields of night-vision, remote sensing, optical communications, and emerging medical imaging modalities [1–4]. Silicon (Si) has been widely used in the mid-infrared and far-infrared imaging due to its optical properties, high hardness, strong chemical stability, and general compatibility with optical coating and micro-fabrication processing [3–5]. Unfortunately, the refraction index of Si in the IR regions is quite high ($n = 3.3$), which leads to large reflection losses.

The resulting IR spectral transmittance (50–60%) degrades their broad band transparent property, good hydrophobicity, great in-oxidizability and high-k gate dielectric [2,11–17]. Furthermore, the refraction index of HfO$_2$ is about 1.9 (0.6–12 µm), which is suitable to be used as ARC for Si [2,11,18–20].

Herein, we prepared HfO$_2$ films as the anti-reflection coatings on double-sided Si substrate (HfO$_2$/Si/HfO$_2$) to reduce the IR reflection by using reactive direct current magnetron sputtering (DCMS) method. Ultra-high IR transmittance of (99% at 6.6 µm) had been obtained. Furthermore, the position of the transmittance peak of the films can be regulated by adjusting the thickness of HfO$_2$ films in the range of 4.2–8.1 µm. In addition, the HfO$_2$ films showed good hydrophobicity with the wetting angle of 101° to 128°. The HfO$_2$/Si/HfO$_2$ samples are easy to fabricate for their simple structure and the study exhibit prospective applications for in IR optical areas, such as atmospheric detection, aerospace, and civilian production.
2. Experimental and simulation methods

2.1. Preparation of the HfO$_2$ films

HfO$_2$ films were deposited by DCMS (MS650C, KYou, China). The chamber was initially evacuated to $2.1 \times 10^{-8}$ Pa, and high purity Ar (99.99%) and O$_2$ (99.99%) were introduced during deposition. The flow rate of Ar and the O$_2$ were 80 sccm and 4 sccm, respectively. A Hf target with a diameter of 76.2 mm and a purity of 99.995% was used to prepare the HfO$_2$ film. The Hf target was sputtered in an argon atmosphere for 10 min to remove the surface oxide before deposition. The fused silica and p-type (100) silicon wafer were used as substrates, and the HfO$_2$/SiO$_2$ samples were mainly used for studying UV–VIS–NIR transmittance and calculating optical thickness. A standard chemical cleaning was performed on the substrates. Especially, the silicon wafers were precleaned with a Piranha solution to remove the native oxide. The deposition temperature and time were adjusted to optimize the crystallinity and thickness of the HfO$_2$ films. The detailed parameters of the sputtering process were listed in Table 1.

2.2. Materials characterization

The crystal structure of the HfO$_2$ film was measured by an X-ray diffraction instrument (XRD, PANalytical B.V., Model Xpert Pro) with Cu-K$_\alpha$ radiation ($\lambda = 0.15406$ nm). Jade 6.5 software was used to investigate crystal structure and analyze the grain size. The Hf and O element were detected by X-ray photo-electron spectroscopy (XPS, PHI 5700 ESCA System). The XPS data were analyzed by using Casa software. The adventitious carbon (AdC) was used to correct the binding energy scale. A scanning electron microscope (SEM, SUPRA 55 SAPHIRE) was used to confirm the morphology and the thickness. A standard chemical cleaning was performed on the substrates. Especially, the silicon wafers were precleaned with a Piranha solution to remove the native oxide. The deposition temperature and time were adjusted to optimize the crystallinity and thickness of the HfO$_2$ films. The detailed parameters of the sputtering process were listed in Table 1.

2.3. Simulation methods

The antireflection AR is used widely to reduce the reflection losses at the interfaces between two optical media [23,24]. The ideal condition of a single anti-reflection layer is based on eliminating the mismatch of the refraction index. And it should be satisfied with the following equation:

$$n_1 = \sqrt{n_0 n_2}$$  \hspace{2cm} (2)

$$d = \lambda/4 n$$  \hspace{2cm} (3)

where $n_1$, $n_0$, and $n_2$ is the refraction index of the AR layer, air and substrate, respectively, $d$ is the thickness of the anti-reflection layer, and $\lambda$ is the corresponding AR peak wavelength.

In this paper, TFCalc software was used to simulate the anti-reflection structure of the single-sided and double-sided layers. And it assumes the layer is optically isotropic and homogeneous with the plane and parallel faces, the reflectance and transmittance of the single-sided structure and double-sided structure can be obtained by the TMM method [9,25]. The refractive index ($n$) and extinction coefficient ($k$) of the Si and HfO$_2$ from the references [26] are used as the parameters for the simulation of the single-sided and double-sided structure systems.

3. Results and discussion

3.1. Phase compositions

Phased compositions of the HfO$_2$/Si samples (#1–#5) were characterized by XRD analysis. As shown in Fig. 1a, all of the diffraction peaks are belonging to the monoclinic phase according to HfO$_2$ (JCPDS 34-0104) [27,28], and there are three dominant diffraction peaks of (011), (−111), (020) crystal planes. The crystal structure adopts a monoclinic structure with space group P2$_1$/c (Fig. 1b) [29–31]. As the deposition temperature increasing, the dominant peak intensity is enhanced, and the intensity of the diffraction peaks of (−111) and (020) reach the maximum for sample deposited at 400 °C (#4). However, the intensity of the dominant diffraction peak decreased slightly when the deposition temperature increased to 500 °C, which may be attributed to the densifying of the sample. The result indicates that obvious crystallization at higher deposition temperature.

The surface chemical composition and valence states of the HfO$_2$/Si deposited at 400 °C (#4) were investigated by XPS analysis. As shown in Fig. 2a, the deconvolution peak of Hf 4f can be resolved into two components of 16.0 eV and 17.7 eV, which can be attributed to Hf 4f$_{5/2}$ and Hf 4f$_{7/2}$ of Hf$^{4+}$, respectively [2]. Besides, the deconvolution peak of O 1s suggests two type states of O element on the surface (Fig. 2b), which may be relative to the Hf-O bonding and adsorbed oxides [2,29]. No lower valence of Hf could be detected in the sample, suggesting that Hf is sufficiently oxidized during the deposition process.
3.2. Surface morphology

The surface morphology and thickness of HfO$_2$/Si were investigated by SEM. As shown in Fig. 3, the samples are smooth and crack-free, and are composed of dense irregular grains with uniform size distribution. Besides, the grain sizes of samples (#1–#4) are about 100–200 nm (Fig. 3a–d), except for sample #5, which exhibits smaller grain size in dozens of nanometers (Fig. 3e). Furthermore, the thickness of the samples is presented in the insets of SEM images. The thickness of the films decreases from 1390 nm to 920 nm as deposition temperature increasing, due to easily occurred migration and rearrangement of the sputtering particles at higher substrate temperature [32,33].

AFM measurement (2 × 2 µm) of the HfO$_2$ films was carried out to further understand the surface morphology of the films. As shown in Fig. 4, the films are consist of large grains with a diameter of 100–250 nm, which is in consistent with the SEM results. The roughness of samples is small (Table S1), and the difference in roughness can be neglected considering the thickness of samples.

3.3. Optical performances

The spectral transmittance of HfO$_2$ films on fused silica (HfO$_2$/SiO$_2$) and silica substrate (HfO$_2$/Si) was measured from 250 to 2500 nm and 2.5 to 25 µm, respectively (Fig. 5). It seems that the samples exhibited high transmittance at 500–2500 nm (Fig. 5a). And the slight decrease of transmittance (250–500 nm) may be due to the large thickness of samples. Besides, it is obvious that the interference phenomena between HfO$_2$ films and substrate, which develops oscillations in the spectrum of transmittance, leading to the transmittance peak of 94% and transmittance valley of 70% at ranges from 500 to 2500 nm [32–35]. Meanwhile, the difference in transmittance spectra may be caused by the differences in the thickness of the films. The optical thickness of the samples was also calculated by the envelope method from the transmittance curves [21,22]. As shown in Fig. S1, the optical thickness is in good agreement with SEM results.

The IR transmittance spectra of HfO$_2$/Si samples (#1–#5) were shown in Fig. 5b. It seems that the transmittance was attenuated at longer wavelengths. The interference can be identified at 2.5–12 µm waveband, where absorption in both the HfO$_2$ films and the silica substrate is negligible. And the transmittance peaks exceeded 70% at 3–5 µm and 8–14 µm, which is higher than the IR transmission of Si wafer (~ 60%). Besides, the transmittance peak shifted to the short wavelength as the temperature increased, which is mainly due to the decrease of the film thickness. However, the interference fringes have vanished at a longer wavelength. The lower transmittance from 12 to 25 µm can be assigned to the lattice vibration absorption of the HfO$_2$ films, which gives rise to an increase of reflection [11,28]. Although the HfO$_2$ film is thick, the absorption of Si substrate can be
clearly distinguished between 12.5 and 20 µm. Note that measurements close to the cut off wavelength of 25 µm are also subject to large uncertainties.

3.4. IR optical performances of double-sided HfO$_2$ films (HfO$_2$/Si/HfO$_2$)

In general, single-sided anti-reflection film can only reduce the reflection loss of one layer of the interface and it is difficult to achieve the ideal anti-reflection effect. The HfO$_2$/Si/HfO$_2$ films were fabricated to further increase the infrared transmittance and reduce the reflection loss at both sides of the dielectric interfaces. The anti-reflection effect schematic illustration for the single-sided and double-sided structures was shown in Fig. 6a. As shown in Fig. 6b, all the HfO$_2$/Si/HfO$_2$ samples show higher transmittance and lower reflectance at the wavelength range of 2.5–12 µm, for the reason that HfO$_2$ films can reduce the reflection by impedance matching between the interface of Si substrate and air on double sides. Furthermore, the positions of the transmittance peak (4.2–8.1 µm) can be regulated by adjusting the thickness of the HfO$_2$ films according to the condition for optimal anti-reflection effect of single-layer coating. Besides, the regulation waveband and the IR peak transmittance of previous studies, and this work are shown in Table S2. It seems that the double-sided HfO$_2$ films exhibit a comparable IR transmittance, which is favorable to the practical application.

The IR spectra of single-sided and double-sided samples under the same preparation condition (#4 and #9) were compared with that of base silicon of Si substrate, and the corresponding IR transmittance and reflectance were shown in Fig. 7a. Compared with the
Si substrate, the IR transmittance of HfO$_2$/Si and HfO$_2$/Si/HfO$_2$ samples are significantly increased at about the wavelength range of 2.5–12 µm. And the corresponding reflectance spectrum is obviously exhibited an anti-reflection effect compared to Si substrate. The transmittance of the HfO$_2$/Si/HfO$_2$ (#9) is enhanced to 99%, which is nearly 40% and 30% higher than that of the bare silicon wafer and HfO$_2$/Si (#4), respectively. To further clarify the underlying physics, the simulations are carried out for the single-sided and double-sided systems. The actual thickness is consistent with the simulated thickness, and the thickness of HfO$_2$ film and Si substrate is 1 µm and 300 µm, respectively. As shown in Figs. 7a and S3, the experimental results are well-coincident with the simulated results.

To further verify the practicability of the double-sided HfO$_2$ films, the IR thermal image was performed to visually illustrate the anti-reflection effect. The HIT letters were written on the aluminum sheet by black carbon pen, and the aluminum sheet was covered with silicon wafers, single-sided and double-sided plating samples (#4 and #9). As shown in Fig. 7b, the IR temperature of the samples was basically the same at room temperature, and they slightly revealed the underlying words of ‘HIT’. One point was worthy to mention that the IR temperature presented by the thermal image was related to emissivity and temperature. When the temperature was at room temperature, the thermal radiation of samples was negligible in the environment, resulting in a tiny difference of IR temperature. When the heating wafer was heated to 120 °C, the words of ‘HIT’ were clearly observed from the IR thermal image (Fig. 7c). The words on Al infrared temperature was increased to 87.9 °C due to the high emissivity of black carbon materials. For the other three samples, the clarity of the ‘HIT’ logo gradually increased from B to D. The main reason was that HfO$_2$ films not only possessed the great IR anti-reflection effect on silicon substrate, its absorption also increased significantly in the waveband of 12–25 µm [11,26,36]. Besides, the temperature of HfO$_2$/Si/HfO$_2$ is about 3.8 °C higher than that of HfO$_2$/Si and 9.5 °C higher than that of Si, which was easier to increase the detection sensitivity in IR detection. The results indicate that the double-sided samples own excellent anti-reflection effect, which possesses great significance for the development of IR optics.

3.5. Hydrophilic behavior

Since the samples with good hydrophilicity could be better applied under harsh serving environments, the contact angles of HfO$_2$/Si (#1–#5) were measured, and the results were shown in Fig. 8. The water contact angles of the HfO$_2$ films deposited from 200°C to 500°C (#2–#5) are between 101° and 105°, while the film prepared at room temperature has a larger contact angle of 128°. Since hydrophobicity is also dependent on the chemical composition and structure [18,37], it seems that higher deposited temperature (above 200°C) could enhance the water adsorption due to crystallinity of the films, resulting in decreased wetting performance [18,38–40]. The results indicate that the HfO$_2$ film has a good ability to serve in
the special environment and is beneficial to the detection of infrared signals due to its hydrophobicity.

4. Conclusions

The double-sided anti-reflection HfO₂ films on Si substrate were successfully fabricated by means of DCMS technology. And the films prepared at different substrate temperatures showed monoclinic poly-crystalline with flat surface morphology. The single-sided samples showed a good anti-reflection effect at mid-IR (2.5–12 µm). Furthermore, the peak infrared transmittance of double-sided HfO₂ film could be up to 99%, which increased by 40% than that of bare Si. Besides, the HfO₂ films on Si substrate not only have an anti-reflection effect but also can provide better anti-humidity and environmental stability with the water contact angle from 101° to 128°. These important findings offer a new way to enhance IR anti-reflection of silicon substrate, which will have a prospective application in infrared optical fields.

CRediT authorship contribution statement

Jiupeng Zhao, Shuliang Dou and Yao Li conceived the idea, designed the experiments and revised the paper. Jinxin Gu fabricated the samples, finished the test date and prepared the manuscript with Hang Wei and Feifei Ren. Qingpu Fan, Gaoping Xu, Xi Chen and Shanshan Song coordinated this study. This article was discussed with contributions from all authors. All authors have approved the final version of this article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

The roughness parameters of single-sided layer of HfO₂ films, the optical and actual thickness at different deposition temperatures, the surface micro-structure of double-sided film deposited different
time, and the regulation waveband and the infrared peak transmittance of previous studies and this work. Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2020.158337.

References


