**Hf$_{1-x}$Si$_x$O$_2$ Nanocomposite Coatings Prepared by Ion-Assisted Co-Evaporation Process for Low-Loss and High-LIDT Optics**

Hongfei Jiao $^{1,2}$*, Xinshang Niu $^{1,2}$, Jinlong Zhang $^{1,2}$, Bin Ma $^{1,2}$, Xinbin Cheng $^{1,2}$ and Zhanshan Wang $^{1,2}$

1. Key Laboratory of Advanced Micro-Structured Materials, Ministry of Education, Shanghai 200092, China; 1810081@tongji.edu.cn (X.N.); jinlong@tongji.edu.cn (J.Z.); mabin@tongji.edu.cn (B.M.); chengxib@tongji.edu.cn (X.C.); wangzs@tongji.edu.cn (Z.W.)

2. Institute of Precision Optical Engineering, School of Physics Science and Engineering, Tongji University, Shanghai 200092, China

* Correspondence: jiaohf@tongji.edu.cn

**Abstract:** Hf$_{1-x}$Si$_x$O$_2$ nanocomposites with different SiO$_2$ doping ratios were synthesized using an ion-assisted co-evaporation process to achieve dense amorphous Hf$_{1-x}$Si$_x$O$_2$ coatings with low loss and a high laser-induced damage threshold (LIDT). The results showed that the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites ($x \geq 0.20$) exhibited excellent comprehensive performance with a wide band gap and a dense amorphous microstructure. High-temperature annealing was carried out to ensure better stoichiometry and lower absorption. Precipitation and regrowth of HfO$_2$ grains were observed from 400 °C to 600 °C during annealing of the Hf$_{0.80}$Si$_{0.20}$O$_2$ nanocomposites, resulting in excessive surface roughness. A phenomenological model was proposed to explain the phenomenon. The Hf$_{1-x}$Si$_x$O$_2$ nanocomposites ($x = 0.3$ and $0.4$) maintained a dense amorphous structure with low absorption after annealing. Finally, a 1064-nm Hf$_{0.70}$Si$_{0.30}$O$_2$/SiO$_2$ high-performance reflector was prepared and achieved low optical loss (15.1 ppm) and a high LIDT (67 J/cm$^2$).

**Keywords:** Hf$_{1-x}$Si$_x$O$_2$ nanocomposites; ion-assisted co-evaporation process; annealing; dense amorphous structure; low optical loss; high LIDT

1. Introduction

Optical coatings are enabling technologies for advanced laser systems, such as laser fusion facilities [1], gravitational wave detection systems [2], and ultra-short and ultra-intense lasers [3]. Their performance is highly dependent on the properties of the low- and high-index materials that constitute the multilayer coatings. It is desirable for the coating material to have a dense amorphous microstructure with low loss [4–6], a wide bandgap [7], and a high LIDT [8]. The low-index material SiO$_2$ that is appropriately prepared using energetic deposition meets all the above requirements [9]. However, it is difficult to obtain high-index material with excellent comprehensive properties. Ta$_2$O$_5$ films prepared using energetic deposition exhibit a fine and dense amorphous microstructure with low loss [10,11]. However, the bandgap of Ta$_2$O$_5$ is narrow, resulting in unsatisfactory laser damage resistance [11]. By contrast, HfO$_2$ has a superior bandgap and LIDT [12] and is widely used in coatings for high-power lasers at facilities such as the National Ignition Facility [13] or Laser MegaJoule [14]. Nonetheless, it is still quite challenging to obtain a dense and amorphous microstructure of HfO$_2$ with extremely low absorption and scattering loss.

Two approaches have been proposed to modify the HfO$_2$ properties to improve its performance. In nanolamination, thin amorphous layers are added to HfO$_2$ coatings to suppress crystallization during HfO$_2$ growth and achieve a smooth surface with low scattering loss [15]. However, this method fails to adjust the bandgap, and the numerous interfaces in the nanolaminate reduce the LIDT, electrical property, and thermal conductivity. The fabrication of nanocomposites is another approach in which amorphous material, such as...
Materials 2021, 14, 2606

SiO₂, is doped with HfO₂ to modify its structural, optical, and electrical properties dramatically. Several works already demonstrated the high potential of HfO₂-SiO₂ nanocomposite coating applications.

Ion beam sputtering (IBS) technology has been widely used for the deposition of mixtures of HfO₂ and SiO₂ because it enables the formation of dense nanocomposites with high stability and repeatability. For instance, Jensen et al. [16–18] experimentally demonstrated that mixed HfO₂ with SiO₂ prepared by IBS can effectively reduce film absorption and promote LIDT for nanosecond and femtosecond pulses. Abromavicius et al. [19] studied the effects of high temperature annealing on the spectral, microstructural and LIDT properties of sputtered HfO₂ and HfO₂-SiO₂ mixture-based ultraviolet (UV) mirrors, demonstrating the high potential of HfO₂-SiO₂ nanocomposites for the modifications of LIDT, absorption and surface topography. However, investigations of the optical loss of co-sputtered Hf₁₋ₓSiₓO₂ nanocomposites have been rare. Moreover, the IBS process is not suitable for the preparation of large-size optical components, because the area of the target material bombarded by the ion beam is too small, resulting in poor film thickness uniformity in the preparation of large-size optical elements; additionally, the fabrication cost is relatively high.

Many studies have focused on the HfO₂-SiO₂ nanocomposites fabricated by electron beam evaporation (EB). For example, Jena et al. [20] performed a detailed investigation of the optical properties and laser damage threshold of HfO₂-SiO₂ nanocomposites. It was observed that the roughness, bandgap, and LIDT of HfO₂ are dramatically improved by the addition of SiO₂. Tokas et al. [6] reported on the morphological evolution and analyses of the HfO₂-SiO₂ nanocomposites at various mixing compositions and concluded that the HfO₂-SiO₂ binary composite system has great potential for ultraviolet optical coating applications that require a thin film microstructure with low light scattering. Zeng et al. [21] demonstrated the potential of the HfO₂-Al₂O₃ and HfO₂-SiO₂ nanocomposites in improving the LIDT of dichroic laser mirrors. However, the coatings prepared by the EB process have a porous and loose microstructure that gives rise to a high scattering loss and poor environmental stability [22].

By contrast, the ion-beam assisted deposition (IAD) process may have greater potential for the fabrication of low-loss laser films, because high-energy ion bombardment will increase the packing density of the HfO₂ films. The issue is more complicated and quite challenging for obtaining low absorption, amorphous and high-LIDT HfO₂ prepared by IAD, because HfO₂ films prepared by IAD always show a polycrystalline and rough microstructure [23] and high absorption [24]. The use of HfO₂-SiO₂ nanocomposites only solves some of these issues of HfO₂ films prepared by IAD, and annealing is always needed to improve the performance. However, detrimental phenomena such as recrystallization may occur during annealing, leading to a loss of the desired properties [25,26].

To the best of our knowledge, no systematic studies on the HfO₂-SiO₂ nanocomposite coatings have been performed to date and, in particular, excellent comprehensive performance with low optical loss, a wide bandgap, and a high LIDT has not been achieved. Additionally, very few studies have focused on the optical properties of the HfO₂-SiO₂ mixture prepared by ion-assisted co-evaporation process and the total optical loss of the HfO₂-SiO₂ mixture. The interrelationship between the crystallization, microstructure, and absorption of HfO₂-SiO₂ nanocomposite coatings prepared by the ion-assisted co-evaporation process before and after annealing is the core issue of the present study.

In this work, a systematic study was designed to find a suitable approach to fabricate high-performance coatings characterized by low absorption, low scattering, and a high LIDT simultaneously. We systematically clarified the relationships between the SiO₂ content and the refractive index, extinction coefficient, bandgap, and crystal phase structure and analyzed the evolution of the absorption and microstructure at different annealing temperatures and SiO₂ doping ratios. HfO₂-SiO₂ nanocomposites with a high LIDT and low optical loss can be used in a wide range of applications in high-power laser systems, laser gyroscopes and gravitational wave detection. Additionally, due to
their dense and amorphous film structure, they may enable the development of various promising applications such as high-power laser cavities used underwater, light detection and ranging exposed in outer space and other optical elements used in harsh environments. The experimental details are described in Section 2. Section 3 reported on the evolution of the characteristics of the mixed coatings and provides an example application of the Hf\(_{1-x}\)Si\(_x\)O\(_2\) nanocomposites. A summary of our findings is presented in Section 4.

2. Materials and Methods

2.1. Sample Preparation and Annealing Methods

Five Hf\(_{1-x}\)Si\(_x\)O\(_2\) nanocomposites with a thickness of about 300 nm were prepared with SiO\(_2\) doping ratios from 0% to 40%, where x represents 0, 0.1, 0.2, 0.3, and 0.4. The substrates used in this study were super-polished fused silica. The coating chamber was a modified Optorun OTFC-1300 box coater (Tokyo, Japan). The schematic diagram of the ion-assisted co-evaporation process is shown in Figure 1. Two 10-kW electron-beam guns were located at opposite sides of the chamber, and two shield plates were placed between the two guns to avoid cross-contamination. A 17-cm diameter radio frequency (RF) ion source was installed between the two guns to adjust the atomic energy of the material during the evaporation. A quartz crystal monitor was used for each gun to monitor the evaporation rate. The evaporation rate of each gun was controlled by a computer through the feedback signal from the quartz crystal monitor. A third quartz crystal monitor located in the center of the dome was used to monitor the coating’s total evaporation rate and thickness. After the modification of the coater, the two materials can be deposited simultaneous, and the Hf\(_{1-x}\)Si\(_x\)O\(_2\) nanocomposite coatings were fabricated by controlling the two e-beam guns. A change in composition was achieved by changing the deposition rates of the two materials. The proportional, integral, and differential parameters of the thickness, as well as the process control systems, were judiciously optimized to suppress unwanted fluctuations in the evaporation rate. The baseline vacuum level was 3 × 10\(^{-4}\) Pa, and the substrate temperature was 200 °C. The evaporation sources included 99.95% pure Hafnium metal rods provided by Grinm Group Corporation Limited (Beijing, China) in the right crucible and 99.99% pure SiO\(_2\) particles provided by Feilihua Shichuang Technology Co., Ltd., Shanghai, China in the left ring crucible. We increased the current and voltage of the ion beam-assisted deposition to 1000 mA and 1100 V, respectively, to reduce the porosity and increase the packing density of the film.

![Figure 1. The schematic diagram of the ion-assisted co-evaporation process.](image-url)
heating rate was 5 °C/min from the room temperature to the annealing temperature and natural drop in the aerosphere was used as the cooling process.

2.2. Characterization

The reflectance and transmittance spectra of the samples were measured in the range 190–1300 nm at a close to normal angle of incidence by a spectrophotometer (Cary 5000, Varian, Palo Alto, CA, USA), and the refractive index, extinction coefficient, and thickness of the films were deduced from the spectra using Optichar, the optical characterization software (version 9.96) from Opitlayer (OptiLayer GmbH, Garching, Free State of Bavaria, Germany) [27]. The precision of the optical constants and film thickness was estimated at ±0.01 for the refractive index and ±0.0001 for the extinction coefficient [28]. The optical bandgap of the films was determined using the Tauc algorithm [20,29].

The crystal phase microstructure was determined by an X-ray diffractometer (XRD, Rigaku, Tokyo, Japan), and Cu Kα (λ = 0.15405 nm) and Ni were used as the target material and filter, respectively. The tube voltage and current were 40 kV and 100 mA, respectively, and the scanning speed was 2°/min at a scanning angle ranging from 20° to 80°. Atomic force microscopy (AFM, Bruker, Madison, WI, USA) measurements were performed to determine the surface topography of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites before and after annealing. The three-dimensional AFM images were obtained in the ScanAsyst mode using a Bruker Dimension Icon atomic force microscope (Bruker, Madison, WI, USA). The scan line consisted of 512 points, and the scan areas were 20 µm × 20 µm. Each sample was tested at three different surface positions to confirm the uniformity of the sample. For different positions of the same sample, the surface morphology was consistent and the variation in the surface roughness was within 0.2 nm. The typical and clearest atomic force map was chosen to describe the surface morphology and the average of the three surface roughness values was used to describe its final surface roughness. Photo-thermal technology was used to evaluate the absorption of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites before and after annealing. The wavelength of the pump beam was 1064 nm. The average absorption of the coatings was derived from four 0.5 mm × 0.5 mm areas of each sample.

3. Results

3.1. Optical Properties

We first describe the results of the refractive index and extinction coefficient analyses of the sets of Hf$_{1-x}$Si$_x$O$_2$ nanocomposites. The obtained refractive index and extinction coefficient dispersion curves are shown in Figure 2 indicating that the effects of doping different volume fractions of SiO$_2$ on the refractive index variable and on the extinction coefficient of the ultraviolet band were significant. Both the refractive index and extinction coefficient show a normal dispersion and decrease with an increase in the SiO$_2$ content since silica has a lower refractive index and is less absorptive than hafnia. However, the refractive index spectra show that the refractive index of the Hf$_{0.90}$Si$_{0.10}$O$_2$ nanocomposites is slightly higher than that of the pure HfO$_2$ film in some spectral bands. The reason is that in these composites, the local structure and microstructural evolutions play a relatively large role in the dielectric functions. On the one hand, the addition of low refractive index SiO$_2$ materials will cause a decrease in the refractive index and a decrease in the extinction index. On the other hand, the bond lengths of Hf-Hf and Hf-O are shorter for the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites than the pure HfO$_2$ film, resulting in a denser structure with smaller grains and a higher refractive index [20,30]. The combination of these two mechanisms led to the evolution of the refractive index of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites. This demonstrates the advantages and potential of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites in tailoring the refractive index and decreasing the extinction coefficient of the ultraviolet band. It has to be pointed out that the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites has a lower refractive index compared with pure HfO$_2$, which will limit their application in certain scenarios.
The trend of the bandgaps and SiO$_2$ content shown in Figure 3 indicate that the bandgaps increased gradually with the increase in the SiO$_2$ content. The maximum bandgap of the Hf$_{0.60}$Si$_{0.40}$O$_2$ nanocomposite was 6.01eV. It is commonly recognized that if the bound electrons in the forbidden band absorb enough photon energy, they will be excited to the conduction band, leading to multiphoton ionization, which is the prerequisite for laser damage. The wider the band gap between the forbidden band and the conduction band, the more photon energy should be absorbed during this process, and the higher the LIDT [7,31]. Therefore, these results demonstrate the advantages and potential of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites in improving the bandgap and increasing the damage threshold.

3.2. Microstructure Properties

The X-ray diffraction (XRD) measurements revealed the crystalline states of different SiO$_2$ concentrations, as indicated in Figure 4. It was assumed that the HfO$_2$ film changed from polycrystalline to amorphous with increasing SiO$_2$ content. The as-deposited pure HfO$_2$ coating and Hf$_{0.90}$Si$_{0.10}$O$_2$ nanocomposite coatings exhibited polycrystalline characteristics, and the films contained the monoclinic phase of HfO$_2$ with the preferred (111) orientation [32]. Moreover, the diffraction peaks in the XRD patterns of Hf$_{0.90}$Si$_{0.10}$O$_2$ were slightly less intense than those of the as-deposited pure HfO$_2$ coating. With the further increase in the SiO$_2$ content, no XRD peak was found in the XRD patterns of the

Figure 2. Refractive index (a) and extinction coefficient (b) dispersion curves of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposite with different SiO$_2$ contents.

Figure 3. Bandgap of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposite with different SiO$_2$ contents.
as-deposited Hf$_{0.80}$Si$_{0.20}$O$_2$, Hf$_{0.70}$Si$_{0.30}$O$_2$, and Hf$_{0.60}$Si$_{0.40}$O$_2$ nanocomposites. Broad and amorphous-like patterns without visible peaks indicated the amorphous nature of the thin films. The XRD results revealed that the material composition of the prepared coatings strongly affected the crystal growth of the coating. The higher the SiO$_2$ concentration in the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites, the higher was the resistance to crystallization [22]. The inhibition of crystallization was attributed to the fact that SiO$_2$-doped HfO$_2$ films produce many nucleation sites, preventing the growth of the crystalline phase [33–35]. Another reason is that Hf and Si have different ionic radii, inhibiting the formation of a long-range order structure [36].

Figure 4. X-ray diffraction (XRD) spectra of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites with different SiO$_2$ contents.

The dependence of crystallization on the concentration of SiO$_2$ in the as-deposited Hf$_{1-x}$Si$_x$O$_2$ coating has been presented as above. A SiO$_2$ concentration of 20% or higher was sufficient to achieve a dense amorphous microstructure. High-temperature annealing was carried out to ensure better stoichiometry and lower absorption. In the following subsection, we discuss the evolution of the microstructure and surface roughness of the nanocomposites with different SiO$_2$ contents and annealed at different temperatures. Several interesting trends were observed. The AFM maps of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites before and after annealing are shown in Figure 5. It is worth mentioning that the surface morphology of all samples at the annealing temperature of 300 °C was almost the same as that of the unannealed samples; thus, we only show typical AFM diagrams of the as-deposited samples and those annealed at 400 to 600 °C. The root mean square (RMS) roughness values of the films determined from the topographic images are listed in Table 1.

Table 1. The roughness values of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites coatings annealed at different temperatures.

| Annealing Temperature | Roughness (nm) |
|-----------------------|----------------|
|                       | X = 0 | X = 0.10 | X = 0.20 | X = 0.30 | X = 0.40 |
| As deposited          | 3.92  | 2.63    | 0.153    | 0.186    | 0.203    |
| 300 °C                | 3.68  | 2.54    | 0.173    | 0.201    | 0.218    |
| 400 °C                | 3.83  | 2.59    | 0.12    | 0.232    | 0.201    |
| 500 °C                | 3.88  | 2.61    | 0.191    | 0.197    | 0.197    |
| 600 °C                | 3.75  | 2.35    | 0.225    | 0.216    |           |

We first discussed the evolution of the microstructure and surface roughness of the as-deposited nanocomposites with different SiO$_2$ contents. In the AFM map, we observed in Figure 5a1 that the as-deposited pure HfO$_2$ coatings exhibited a polycrystalline structure composed of small spiky grains. These visible grains enhanced the roughness of the surface; therefore, the as-deposited pure HfO$_2$ coatings had a high surface roughness of 3.92 nm. A further increase in the SiO$_2$ amount inhibited the crystallization and resulted in
a decay of the particles, as shown in Figure 5b. As a result, the as-deposited Hf$_{0.90}$Si$_{0.10}$O$_{2}$ nanocomposites had a slightly lower roughness value (2.63 nm) than the pure HfO$_2$. Moreover, the surface of the amorphous Hf$_{0.80}$Si$_{0.20}$O$_2$, Hf$_{0.70}$Si$_{0.30}$O$_2$, and Hf$_{0.60}$Si$_{0.40}$O$_2$ nanocomposites shown in Figure 5c, respectively, did not consist of visible particles and grains. Thus, they had a surface roughness of less than 0.2 nm and were smoother than the other as-deposited thin films, indicating the lowest scattering loss. This result is consistent with the XRD evolution.

We then investigated the evolution of the microstructure and surface roughness of the nanocomposites annealed at different temperatures. After high-temperature annealing, the microstructure of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites with different SiO$_2$ concentrations exhibited different evolution patterns. High-temperature annealing didn’t change the surface morphology and roughness of the pure HfO$_2$ and Hf$_{0.90}$Si$_{0.10}$O$_2$ nanocomposites, as shown in Figure 5a. By contrast, precipitation and regrowth of the HfO$_2$ grains were observed in Hf$_{0.80}$Si$_{0.20}$O$_2$ nanocomposites annealed at 400 to 600 °C (Figure 5c). The aggregation of smaller grains into larger grains resulted in the uniform distribution of the nano-clusters in the whole field of view of these samples, significantly increasing the surface roughness. When the annealing temperature reached 400 °C, the RMS roughness increased abruptly to 6.12 nm, which was one order higher than that of the other samples. When the annealing temperature reached 500 and 600 °C, the

![Figure 5. Surface morphologies of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites annealed at different temperature.](image-url)
RMS roughness of the nanocomposite reached about 19.1 nm and 25.7 nm, exceeding the usable range of normal optical coatings. As the SiO₂ content increased to 30% and 40%, the Hf₀.70Si₀.30O₂ and Hf₀.60Si₀.40O₂ nanocomposites maintained a smooth surface morphology with a minimum roughness of less than 0.2 nm, even after 600 °C annealing, as shown in Figure 5d–d₄ and e₁–e₄. Three states were observed in the evolution of the roughness and surface topography before and after annealing: a stable crystalline state, a transition state, and a stable amorphous state. A phenomenological model is proposed to describe the formation of the three different states (Figure 6).

In the first stage, the nanocomposite is in a stable crystalline state when the SiO₂ concentration of the Hf₁₋ₓSiₓO₂ coatings is less than 20% (Figure 6a₁). The deposition of the Hf molecules was completely unordered in the initial period (represented by the white spheres). The SiO₂ molecules (represented by the blue areas) are evenly dispersed between the hafnium oxide molecules. A certain number of SiO₂ molecules act as barriers to the diffusion of the Hf atoms and delay the nucleation and growth of HfO₂ crystallites [37]. The AFM maps (Figure 5) and XRD (Figure 4) results also indicate that the doping of SiO₂ suppressed the crystallization of HfO₂, but crystallization was the dominating trend. Due to the random collisions between the atoms, short-range ordered atom clusters appeared in the coatings (represented by the dark spheres). The coatings crystallized at the base of the atom clusters, and some small fine grains formed in the as-deposited nanocomposite coating. Subsequently, after high-temperature annealing, the grain size remained almost unchanged, as shown in Figure 6a₂. One possible reason for this phenomenon may be that the ordered and stable polycrystalline structure with higher stored energy is not conducive to the recrystallization of the nanocomposite [38]. Thus, the energy of annealing is mainly used to transfer the surface atoms to existing voids and defects, resulting in reduced surface roughness [39], as shown in Table 1. This may be the main reason why the roughness
of the pure HfO$_2$ and Hf$_{0.96}$Si$_{0.10}$O$_2$ nanocomposites was slightly lower than that of the un-annealed samples at the partial annealing temperature. Another possible explanation is that the doped SiO$_2$ may have induced a silicon-rich liquid phase, which acted as a segregation layer at the grain boundaries and grain junctions (represented by the red areas) during annealing. The motion of a moving grain boundary, which is dragged by a segregated solute layer and exhibits lowered mobility, inhibits the recrystallization of HfO$_2$ at the depositing and annealing temperature [40], as shown in Figure 6a$_2$.

Regarding the second stage, the nanocomposite is in a transition state from crystalline to amorphous when the SiO$_2$ concentration of the Hf$_{1-x}$Si$_x$O$_2$ coatings is around 20%, which is a critical state and represents a unique stage in the evolution. As shown in Figure 6b$_1$, more and more SiO$_2$ aggregates occupying an increasing number of nucleation sites were observed (represented by the blue spheres). Additionally, the number of SiO$_2$ molecules surrounding the Hf atoms increased, hindering the diffusion of Hf significantly and ultimately delaying the nucleation and growth of the HfO$_2$ crystallites. No silicon-rich liquid was formed during this process. The 20% SiO$_2$ doping amount was sufficient to completely suppress the crystallization of the as-deposited nanocomposite, resulting in a smooth amorphous structure. However, abnormal crystallization occurred with an increase in the annealing temperature above 400 °C, as shown in Figure 6b$_2$. Small grains were aggregated into large grains because the transition of HfO$_2$ from an amorphous state to the crystalline state usually occurs at approximately 400 °C during annealing [25]. Thus, the amorphous as-deposited Hf$_{1-x}$Si$_x$O$_2$ film did not crystallize when annealing occurred below 400 °C. The most likely reasons for this abnormal evolution pattern are as follows. The amorphous film is in a state of high free energy, which can be lowered by crystallizing into a metastable phase assembly, in which structurally complex phases require extensive atomic rearrangement [41]. Subsequently, annealing at high temperatures provided energy to the Hf atoms, enhancing the diffusion and mobility of the Hf atoms. Amorphous films in the metastable state start to crystallize without being inhibited by a segregation layer. The two mechanisms, i.e., the inhibition of crystallization by doping and the promotion of crystallization during annealing, compete with each other and play a dominant role in the transition state, thereby affecting the balance between preferential growth and random growth. Thus, there is a phase transition from amorphous to polycrystalline, and abnormal grain growth occurs at higher temperatures. Since the clusters are randomly distributed and gradually increase in size, the bulk density of the atoms increases, resulting in larger film stress. The mismatch between the stress of the film and the substrates leads to discontinuous surface topography with several gaps, as shown in the AFM images in Figure 5c$_3$,c$_4$.

In the third stage, the nanocomposite is in a stable amorphous state when the SiO$_2$ concentration of the Hf$_{1-x}$Si$_x$O$_2$ coatings is more than 20%. As shown in Figure 6c$_1$, a sufficient amount of doped SiO$_2$ completely inhibits crystallization by occupying numerous nucleation sites. This occurrence plays a leading role in thermal annealing, and the energy of annealing is not sufficient to cross a potential barrier to induce crystallization. Therefore, all the as-deposited and annealed Hf$_{0.70}$Si$_{0.30}$O$_2$ and Hf$_{0.66}$Si$_{0.40}$O$_2$ nanocomposites maintained an amorphous structure with a smooth surface.

3.3. Absorption at 1064 nm

Table 2 presents the weak absorption at 1064 nm of all Hf$_{1-x}$Si$_x$O$_2$ nanocomposites with different SiO$_2$ contents before and after annealing. As shown in Table 2, the pure HfO$_2$ film had a maximum absorption of 131 ppm. SiO$_2$ doping reduced the absorption of the film substantially, and as the content of SiO$_2$ increased, the absorption gradually decreased. The evolution of the absorption at 1064 nm was almost the same as the evolution of the ultraviolet (UV) extinction coefficient, as discussed in the previous section. The Hf$_{0.66}$Si$_{0.40}$O$_2$ nanocomposite had the lowest absorption (43 ppm). After high-temperature annealing, the absorption decreased significantly with an increase in the annealing temperature for the different Hf$_{1-x}$Si$_x$O$_2$ nanocomposites. When the annealing temperature reached 600 °C, all
nanocomposite Hf$_{1-x}$Si$_x$O$_2$ coatings, including the pure HfO$_2$ coating, exhibited relatively low absorption at 1064 nm, indicating that the absorption of the Hf$_{1-x}$Si$_x$O$_2$ coatings was generally reduced at high-temperature annealing. However, the Hf$_{0.80}$Si$_{0.20}$O$_2$ coating with the 20% SiO$_2$ concentration had the highest absorption (18.5 ppm) after annealing at 600 °C, which is contrary to the common belief that high-temperature annealing enhances the oxidation of HfO$_2$ films and reduces the absorption loss.

Table 2. The weak absorption at 1064 nm of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposite coatings annealing at different temperature.

| Annealing Temperature | X = 0  | X = 0.10 | X = 0.20 | X = 0.30 | X = 0.40 |
|-----------------------|--------|----------|----------|----------|----------|
| As deposited          | 131.0  | 110.4    | 100.0    | 68.0     | 43.0     |
| 300 °C                | 72.0   | 55.2     | 35.3     | 14.3     | 9.8      |
| 400 °C                | 31.0   | 20.2     | 15.0     | 12.2     | 7.8      |
| 500 °C                | 15.0   | 9.5      | 11.2     | 5.0      | 3.4      |
| 600 °C                | 2.5    | 2.0      | 18.5     | 1.5      | 1.5      |

Since the weak absorption was affected by the combination of defect absorption and the microstructure of the films [42], the combination of substoichiometric defect and structural defect dominant description was used to illustrate the evolution of the weak absorption, as is shown in Figure 7. At annealing below 400 °C, the amorphous as-deposited Hf$_{1-x}$Si$_x$O$_2$ film did not crystallize. The main role of annealing at this stage is to enhance the oxidation degree to achieve better stoichiometry. Thus, it is concluded that the transformation from a substoichiometric to a stoichiometric process in A tends to reduce the optical absorption considerably. This explanation applies to all Hf$_{1-x}$Si$_x$O$_2$ films mentioned above, as shown in Table 1. When the annealing temperature reached around 400 °C, the structure of the Hf$_{0.80}$Si$_{0.20}$O$_2$ nanocomposite began to change from amorphous to crystalline. Although the appearance of grain boundaries during crystal growth resulted in reduced thermal diffusion, the transformation from a substoichiometric to a stoichiometric process was not complete. Therefore, the weak absorption of the Hf$_{0.80}$Si$_{0.20}$O$_2$ nanocomposite continued to decrease after 400 °C annealing in process B. By contrast, abnormal crystallization occurred as the annealing temperature reached 500 °C and 600 °C. Large atom clusters reduced the oxidation degree; thus, not all Hf$^{4+}$ ions could bond with O$^{2-}$ ions. Moreover, numerous grain boundaries also hindered thermal diffusion. The annealed Hf$_{0.80}$Si$_{0.20}$O$_2$ nanocomposite exhibited high absorption in process C.

Figure 7. Weak absorptions of the as-deposited and annealed Hf$_{0.80}$Si$_{0.20}$O$_2$ films at different temperatures. (A–C) represent the evolution of the films in the annealing process.
3.4. Application of the Hf$_{1-x}$Si$_x$O$_2$ Nanocomposites

We have clarified the evolution of the dispersion and bandgap at different silicon oxide doping ratios and determined the evolution of the structure and absorption of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposite coatings during the growth and post-annealing stages. It was found that the SiO$_2$ concentration significantly affected the structure evolution. When the SiO$_2$ concentration exceeded 30%, after post-annealing, the Hf$_{1-x}$Si$_x$O$_2$ nanocomposite fabricated by IAD had an excellent comprehensive performance with a dense amorphous structure, low absorption, low roughness, and a wide bandgap. In addition, the Hf$_{0.70}$Si$_{0.30}$O$_2$ nanocomposite may have better potential applicability because of its higher refractive index. To demonstrate the practicability of these techniques, 1064-nm high reflective coatings consisting of SiO$_2$ and Hf$_{0.70}$Si$_{0.30}$O$_2$ were prepared by the IAD co-evaporation method and annealed at 600 °C. The film structure was sub/(LH) $^*$ 17 L/air, where H and L denote high (Hf$_{0.70}$Si$_{0.30}$O$_2$) and low (SiO$_2$) index coating materials with quarter-wave (QW) optical thicknesses at 1064 nm. The reflectance spectrum measured by a spectrophotometer is shown in Figure 8. It was observed that the reflectance of the fabricated Hf$_{0.70}$Si$_{0.30}$O$_2$/SiO$_2$ high reflective (HR) coating at 1064 nm was higher than 99.9%. Additionally, even though the Hf$_{0.70}$Si$_{0.30}$O$_2$ nanocomposite had a lower refractive index compared to pure HfO$_2$, resulting in a narrower reflection band, the HR coatings still had a sufficiently wide reflection bandwidth to satisfy practical requirements.

![Figure 8](image-url) The experimental reflectance spectrum of the 1064-nm Hf$_{0.70}$Si$_{0.30}$O$_2$/SiO$_2$ high reflective coating.

An Nd:YAG laser operating at 1064 nm with the TEM00 mode was used to measure the LIDT of the final fabricated 1064 nm high reflective coatings. The Q-switched pulse width was 10 ns and the beam diameter was 1 mm in the 1/e$^2$ of the laser energy. The laser damage tests were performed in 1-on-1 mode [43]. Damage was determined by a Nomarski microscope with 200× magnification. The scatterometer (ALBATROSS-TT, Hong Kong, China) was used to measure the angular resolved scatter values (ARS) of the 1064 nm high reflective coatings. The XRD spectra, AFM map, ARS, and typical damage morphology are shown in Figure 9. The absorption loss, surface roughness, scattering loss, and damage threshold are listed in Table 3.

Table 3. Optical properties of the 1064-nm high reflective coatings consisting of SiO$_2$ and Hf$_{0.70}$Si$_{0.30}$O$_2$ after 600 °C annealing.

| Samples                  | Absorption/ppm | Scattering/ppm | Total Loss/ppm | RMS/nm | LIDT/J/cm$^2$ |
|--------------------------|----------------|----------------|----------------|--------|---------------|
| Hf$_{0.70}$Si$_{0.30}$O$_2$–SiO$_2$ HR coatings | 1.8            | 13.3           | 15.1           | 0.225  | 67 ± 2        |
Figure 9. X-ray diffraction (XRD) spectra (a), atomic force microscopy (AFM) map (b), ARS (c), and typical damage morphology (d) of the 1064-nm high reflective coatings consisting of SiO\textsubscript{2} and Hf\textsubscript{0.70}Si\textsubscript{0.30}O\textsubscript{2} after 600 °C annealing.

As depicted in Figure 9a, there were no sharp diffraction peaks in the XRD spectra of the annealed sample, indicating that an amorphous microstructure was maintained during annealing. The surface morphologies illustrated in Figure 9b also showed that the annealed HR coating had a smooth surface with a roughness of 0.225 nm, resulting in a low scattering loss of 13.3 ppm (Figure 9c). Moreover, high temperature annealing effectively reduced its absorption to the level of 1.8 ppm which is comparable to the fused silica substrate, as given in Table 3. The results of absorption loss and scattering loss indicated that the total loss of the HR coating at 1064 nm is as low as 15.1 ppm. The LIDT of the annealed HR coating was 67 J/cm\textsuperscript{2} (Table 3), which was at the same level as the pure HfO\textsubscript{2}/SiO\textsubscript{2} HR coating prepared by EB process [17,44], and the sample exhibited “plasma induced ablation”-type representative damage morphology in the defect free region rather than the nodules induced the catastrophic damage, which reflected the rather high intrinsic damage threshold, corresponding to the low absorption and wide bandgap of the Hf\textsubscript{0.70}Si\textsubscript{0.30}O\textsubscript{2} nanocomposite.

The results demonstrate the excellent comprehensive performance of the nanocomposites with low optical loss, a wide bandgap, a high LIDT and a dense amorphous structure, compared to the HfO\textsubscript{2} film prepared by IBS, EB and IAD [22–24,44]. The material can be successfully prepared using the IAD co-evaporation method and has excellent optical and mechanical properties suitable for laser damage coatings and advanced coating applications.
4. Conclusions

In summary, the characteristics of Hf$_{1-x}$Si$_x$O$_2$ nanocomposites with different SiO$_2$ doping ratios synthesized using an ion-assisted co-evaporation process were systematically investigated, including variation trends of refractive index, extinction coefficient, bandgap, microstructure and absorption loss. The main results can be summarized as follows:

1. For the optical properties, the refractive index and absorption coefficient were found to decrease with increasing silica content from 0% to 40%, except for the anomalous behavior of the compositions with 10% silica in some spectral bands, while the optical bandgap increases monotonically with increasing silica content. This demonstrates the advantages and potential of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites in tailoring the refractive index and increasing LIDT.

2. We analyzed the relationships between the SiO$_2$ content and the microstructure at different annealing temperatures and found that the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites changed from polycrystalline to amorphous with increasing SiO$_2$ content. A SiO$_2$ concentration of 20% or higher was sufficient to achieve a dense amorphous microstructure. The microstructure of the H$_{1-x}$Si$_x$O$_2$ nanocomposites with different SiO$_2$ concentrations exhibited different evolution patterns during annealing. We proposed a phenomenological model to explain the microstructure evolution.

3. We explored the weak absorption at 1064 nm of all Hf$_{1-x}$Si$_x$O$_2$ nanocomposites with different SiO$_2$ contents before and after annealing. SiO$_2$ doping and high-temperature annealing substantially reduced the absorption of the film. When the annealing temperature reached 600 °C, all Hf$_{1-x}$Si$_x$O$_2$ nanocomposites exhibited relatively low absorption. However, the Hf$_{0.80}$Si$_{0.20}$O$_2$ nanocomposites had the highest absorption of 18.5 ppm after annealing at 600 °C. We proposed a description of the substoichiometric defects and the dominant structural defects to illustrate the absorption evolution of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites with different SiO$_2$ contents before and after annealing.

4. When the SiO$_2$ concentration exceeded 30%, a dense amorphous structure with a relatively low roughness value and low absorption loss was maintained after thermal annealing. We prepared 1064 nm high-reflective coatings consisting of SiO$_2$ and Hf$_{0.70}$Si$_{0.30}$O$_2$ and achieved low optical loss (15.1 ppm) and a high LIDT (67 J/cm$^2$).

Our findings demonstrated the great potential of the Hf$_{1-x}$Si$_x$O$_2$ nanocomposites prepared by ion-assisted co-evaporation process for a considerable improvement in LIDT and optical loss. Since these nanocomposites are adopted for optical thin films for the first time in this work, their stress and mechanical loss properties need to be studied in further work. Additionally, further experimental investigations are needed to validate their damage performance and temperature rise under high-energy continuous laser irradiation.

Author Contributions: Conceptualization, H.J., X.N., J.Z., X.C., and Z.W.; methodology, H.J. and X.N.; software, X.N.; validation, H.J., X.N., and J.Z.; formal analysis, H.J. and X.N.; investigation, H.J. and X.N.; resources, H.J., J.Z., X.C., and Z.W.; data curation, H.J. and X.N.; writing—original draft preparation, X.N.; writing—review and editing, H.J., X.N., J.Z., and X.C.; visualization, H.J. and X.N.; supervision, H.J.; project administration, H.J., J.Z., B.M., X.C., and Z.W.; funding acquisition, H.J., J.Z., B.M., X.C., and Z.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Natural Science Foundation of China (No. 61621001, No. 61975155, No. 61925504, No. 61675156); Shanghai Municipal Education Commission (No. 2017-01-07-00-07-E00063); Science and Technology Commission of Shanghai Municipality (No. 17JC1400800); Fundamental Research Funds for the Central Universities.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.
References

1. Moses, E.I. Ignition on the National Ignition Facility: A path towards inertial fusion energy. *Nucl. Fusion* **2009**, *49*, 104022. [CrossRef]
2. Adhikari, R.X. Gravitational radiation detection with laser interferometry. *Rev. Mod. Phys.* **2014**, *86*, 121–151. [CrossRef]
3. Gallais, L.; Cheng, X.; Wang, Z. Influence of nodular defects on the laser damage resistance of optical coatings in the femto-second regime. *Opt. Lett.* **2014**, *39*, 1545–1548. [CrossRef] [PubMed]
4. Zhang, J.; Wu, H.; Jiao, H.; Schröder, S.; Trost, M.; Wang, Z.; Cheng, X. Reducing light scattering in high-reflection coatings through destructive interference at fully correlated interfaces. *Opt. Lett.* **2017**, *42*, 5046–5049. [CrossRef] [PubMed]
5. Tcheliebou, F.; Boyer, A.; Martin, L. Studies on MgO-stabilized zirconia thin films in the UV-visible region. *Thin Solid Film.* **1994**, *249*, 86–90. [CrossRef]
6. Tokas, R.; Sahoo, N.; Thakur, S.; Kamble, N. A comparative morphological study of electron beam co-deposited binary optical thin films of HfO$_2$/SiO$_2$ and ZrO$_2$/SiO$_2$. *Curr. Appl. Phys.* **2008**, *8*, 589–602. [CrossRef]
7. Gallais, L.; Commandré, M. Laser-induced damage thresholds of bulk and coating optical materials at 1030 nm, 500 fs. *Appl. Opt.* **2014**, *53*, A186–A196. [CrossRef]
8. Zhang, X.M.; Wei, X.F.; Li, M.Z.; Yuan, Q.; Wang, W.Y.; Li, F.Q. Bidirectional amplifying architecture with twin pulses for laser fusion facilities. *Laser Phys. Lett.* **2013**, *10*, 115803. [CrossRef]
9. Ouellette, M.F.; Lang, R.V.; Yan, K.L.; Bertram, R.W.; Owles, R.S.; Vincent, D. Experimental studies of inhomogeneous coatings for optical applications. *J. Vac. Sci. Technol. A* **1991**, *9*, 1188–1192. [CrossRef]
10. Masse, J.P.; Szymanski, H.; Zabeida, O.; Amassian, A.; Klemberg-Sapieha, J.; Martinu, L. Stability and effect of annealing on the optical properties of plasma-deposited Ta$_2$O$_5$ and Nb$_2$O$_5$ films. *Thin Solid Film.* **2006**, *515*, 1674–1682. [CrossRef]
11. Wang, L.; Liu, H.; Jiang, Y.; Yang, X.; Liu, D.; Ji, Y.; Zhang, F.; Chen, D. Effects of hot-isostatic pressing and annealing post-treatment on HfO$_2$ and Ta$_2$O$_5$ films prepared by ion beam sputtering. *Optik* **2017**, *142*, 33–41. [CrossRef]
12. Jensen, L.; Mende, M.; Schramey, S.; Jupé, M.; Ristau, D. Role of two-photon absorption in Ta$_2$O$_5$ thin films in nanosecond laser-induced damage. *Opt. Lett.* **2012**, *37*, 4329–4331. [CrossRef]
13. Genin, F.Y.; Stolz, C.J.; Kozlowski, M.R. Growth of laser-induced damage during repetitive illumination of HfO$_2$/SiO$_2$ multilayer mirror and polarizer coatings. *Proc. SPIE* **1997**, *2966*, 273–282.
14. Fornier, A.; Bernardino, D.; Lam, O.; Néauport, J.; Dufour, F.; Schmitt, B.R.; Mackowski, J.-M. High laser damage threshold HfO$_2$/SiO$_2$ mirrors manufactured by sputtering process. In Proceedings of the Third International Conference on Solid State Lasers for Application to Inertial Confinement Fusion, Monterey, CA, USA, 23 July 1999; Volume 3492, pp. 912–920. [CrossRef]
15. Zhong, L.; Daniel, W.L.; Zhang, Z.; Campbell, S.A.; Gladfelter, W.L. Atomic Layer Deposition, Characterization, and Dielectric Properties of HfO$_2$/SiO$_2$ Nanolaminates and Comparisons with Their Homogeneous Mixtures. *Chem. Vap. Depos.* **2006**, *12*, 143–150. [CrossRef]
16. Jensen, L.O.; Mende, M.; Blaschke, H.; Ristau, D.; Nguyen, D.; Emmert, L.; Rudolph, W. Investigations on SiO$_2$/HfO$_2$ mixtures for nanosecond and femtosecond pulses. In Proceedings of the Laser Damage Symposium XLII: Annual Symposium on Optical Materials for High Power Lasers, Boulder, CO, USA, 30 November 2010; Volume 7842, pp. 492–500. [CrossRef]
17. Mende, M.; Jensen, L.O.; Ehlers, H.; Riggers, W.; Blaschke, H.; Ristau, D. Laser-induced damage of pure and mixture material high reflectors for 355nm and 1064nm wavelength. *SPIE Opt. Syst. Des.* **2011**, *8168*, 816821. [CrossRef]
18. Mende, M.; Jensen, L.O.; Ehlers, H.; Bruns, S.; Vergöhl, M.; Burdack, P.; Ristau, D. Applying hafnia mixtures to enhance the laser-induced damage threshold of coatings for third-harmonic generation optics. *SPIE Laser Damage* **2012**, *8530*, 8530W00. [CrossRef]
19. Abromavicius, G.; Kičas, S.; Buzelis, R. High temperature annealing effects on spectral, microstructural and laser damage resistance properties of sputtered HfO$_2$ and HfO$_2$-SiO$_2$ mixture-based UV mirrors. *Opt. Mater.* **2019**, *95*, 109245. [CrossRef]
20. Jena, S.; Tokas, R.B.; Kamble, N.M.; Thakur, S.; Sahoo, N.K. Optical properties and laser damage threshold of HfO$_2$-SiO$_2$ mixed composite thin film. *Opt. Appl.* **2014**, *35*, 850–860. [CrossRef]
21. Zeng, T.; Zhu, M.; Chai, Y.; Li, J.; Shao, J. Dichroic laser mirrors with mixture layers and sandwich-like-structure interfaces. *Photon. Res.* **2021**, *9*, 229. [CrossRef]
22. Cheng, X.; Dong, S.; Zhi, S.; Paschel, S.; Balasa, I.; Ristau, D.; Wang, Z. Waterproof coatings for high-power laser cavities. *Light. Sci. Appl.* **2019**, *8*, 12. [CrossRef]
23. Ai, W.; Xiong, S. Characterization of hafnia thin films made with different deposition technologies. In Proceedings of the XLIII Annual Symposium on Optical Materials for High Power Lasers, Boulder, CO, USA, 22 November 2011; Volume 8190, p. 81900J. [CrossRef]
24. Ma, H.; Cheng, X.; Zhang, J.; Jiao, H.; Ma, B.; Tang, Y.; Wu, Z.; Wang, Z. Effect of boundary continuity on nanosecond laser damage of nodular defects in high-reflection coatings. *Opt. Lett.* **2017**, *42*, 478. [CrossRef] [PubMed]
25. Park, J.-W.; Lee, D.-K.; Lim, D.; Lee, H.; Choi, S.-H. Optical properties of thermally annealed hafnium oxide and their correlation with structural change. *J. Appl. Phys.* **2008**, *104*, 033521. [CrossRef]
26. Jena, S.; Tokas, R.B.; Yao, K.D.; Thakur, S.; Sahoo, N.K. Annealing effects on microstructure and laser-induced damage threshold of HfO$_2$/SiO$_2$ multilayer mirrors. *Appl. Opt.* **2016**, *55*, 6108–6114. [CrossRef] [PubMed]
27. Optilayer. Available online: http://www.optilayer.com (accessed on 18 August 2020).
28. Wang, W.H.; Chao, S. Annealing effect on ion-beam-sputtered titanium dioxide film. *Opt. Lett.* **1998**, *23*, 1417–1419. [CrossRef]
29. Cody, G.D.; Tiedje, T.; Abele, B.; Moustakas, T.D.; Brooks, B.; Goldstein, Y. Disorder and the optical-absorption edge of hydrogenated amorphous silicon. *J. Phys. Colloq.* **1981**, *42*, 301–304. [CrossRef]

30. Das, N.C.; Sahoo, N.K.; Bhattacharyya, D.; Thakur, S.; Kamble, N.M.; Nanda, D. Correlation between local structure and refractive index of e-beam evaporated HfO$_2$-SiO$_2$ composite thin films. *J. App. Phys.* **2010**, *1082*, 023515. [CrossRef]

31. Mero, M.; Liu, J.; Rudolph, W.; Ristau, D.; Starke, K. Scaling laws of femtosecond laser pulse induced breakdown in oxide films. *Phys. Rev. B* **2005**, *71*, 115109. [CrossRef]

32. Liu, F.; Dong, S.; Zhang, J.; Jiao, H.; Ma, B.; Wang, Z.; Cheng, X. Interface and material engineering for zigzag slab lasers. *Sci. Rep.* **2017**, *7*, 16699. [CrossRef]

33. Prajapati, C.S.; Sahay, P.P. Influence of in doping on the structural, optical and acetone sensing properties of ZnO nanoparticulate thin films. *Mat. Sci. Semicond. Proc.* **2013**, *16*, 200–210. [CrossRef]

34. Jiang, S.; He, G.; Gao, J.; Xiao, D.; Jin, P.; Li, W.; Lv, J.; Liu, M.; Liu, Y.; Sun, Z. Microstructure, optical and electrical properties of sputtered HfTiO high-k gate dielectric thin films. *Ceram. Int.* **2016**, *42*, 11640–11649. [CrossRef]

35. Obstarczyk, A.; Kaczmarek, D.; Wojcieszak, D.; Mazur, M.; Domaradzki, J.; Kotwica, T.; Pastuszek, R.; Schmeisser, D.; Mazur, P.; Kot, M. Tailoring optical and electrical properties of thin-film coatings based on mixed Hf and Ti oxides for optoelectronic application. *Mater. Des.* **2019**, *175*, 107822. [CrossRef]

36. Zhang, J.; He, G.; Zhou, L.; Chen, H.; Chen, X.; Deng, B.; Lv, J.; Sun, Z. Microstructure optimization and optical and interfacial properties modulation of sputtering-derived HfO$_2$ thin films by TiO$_2$ incorporation. *J. Alloys Compd.* **2014**, *611*, 253–259. [CrossRef]

37. Louis, B.; Krins, N.; Faustini, M.; Grosso, D. Understanding Crystallization of Anatase into Binary SiO$_2$/TiO$_2$ Sol/Gel Optical Thin Films: An in Situ Thermal Ellipsometry Analysis. *J. Phys. Chem. C* **2011**, *115*, 3115–3122. [CrossRef]

38. Skrotzki, W.; Kegler, K.; Tamm, R.; Oertel, C. Recrystallization of Iron Aluminides. *Mater. Sci. Forum* **2004**, *467*, 525–530. [CrossRef]

39. Khairnar, A.; Mahajan, A. Effect of post-deposition annealing temperature on RF-sputtered HfO$_2$ thin film for advanced CMOS technology. *Solid State Sci.* **2013**, *15*, 24–28. [CrossRef]

40. Wang, J.; Ponton, C.B.; Marquis, P.M. Abnormal grain growth in alumina-doped hafnia ceramics. *J. Mater. Sci.* **1994**, *29*, 3577–3590. [CrossRef]

41. Stemmer, S.; Chen, Z.; Levi, C.G.; Lysaght, P.S.; Foran, B.; Gisby, J.A.; Taylor, J.R. Application of Metastable Phase Diagrams to Silicate Thin Films for Alternative Gate Dielectrics. *Jpn. J. Appl. Phys.* **2003**, *42*, 3593–3597. [CrossRef]

42. Pu, Y.; Qiao, Z.; Zhang, M.; Lu, Z.; Qiu, F.; Lv, L.; Ma, P. Annealing effects on microstructure and laser-induced damage threshold of quasi-rugate filters. *Opt. Express* **2016**, *24*, 23044. [CrossRef]

43. Jiao, H.; Cheng, X.; Liu, Y.; Lu, J.; Ma, B.; He, P.; Wang, Z. The effects of substrate temperatures on the structure and properties of hafnium dioxide (HfO$_2$) films. *Opt. Interf. Coat.* **2010**, *50*, C309–C315. [CrossRef]

44. Niu, X.; Jiao, H.; Bao, G.; Zhang, J.; Cheng, X.; Wang, Z. HfO$_2$-SiO$_2$ mixed film deposited by Ion Assisted Deposition Coevaporation. *Proc. SPIE* **2017**, *10447*, 26.