New design for highly durable infrared-reflective coatings

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The fundamental challenge in designing durable infrared-reflective coatings is achieving the ideal combination of both high reflectivity and durability. Satisfying these competing demands is traditionally achieved by deposition of durable layers on highly reflective metals. We overturn the traditional logic of ‘first reflectivity and then durability’ and propose an alternative of ‘first durability and then reflectivity’: First, a transition-metal compound is selected as a durable base; then its reflectivity is improved by incorporating silver/gold to form an alloy or by overcoating a multilayer stack. Two validation experiments prove that the new strategy works extremely well: the coatings thus obtained have infrared reflectivities close to that of aluminum, and their hardness and acid and salt corrosion resistances are 27–50, 400–1 500 and 7 500–25 000 times that of aluminum. The traditional mirror coating (e.g., Al/SiO2 films) is more suitable for moderate environments, while our mirror coating that was obtained by the new strategy (e.g., an Ag-doped hafnium nitride film) is more suitable for harsh environments, such as ones with dust, windblown sand, moisture, acid rain or salt fog. This work opens up new opportunities for highly durable infrared-reflective coatings and rejuvenates the study of transition metal compounds in a completely new area of optics.

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INTRODUCTION

Recently, there has been an increasing need for durable infrared-reflective coatings on large infrared telescopes1–7, night-vision systems3, pointing and tracking systems3 and other optical systems4–7. The ideal durable infrared-reflective coatings require not only high reflectivity in a particular infrared band but also durability to resist scratches and corrosion damage from long-term environmental exposure in environments with dust, windblown sand, moisture, acid rain and salt fog8–10. Unfortunately, ideal durable infrared-reflective coatings are hard to obtain, as reflectivity and durability are a classical dilemma to some extent, difficult to obtain simultaneously. In Al, for example, the abundance of free electrons renders an excellent infrared reflectivity, but the electrons and the metallic bonds result in high corrosion and a low hardness, leading to a poor durability8,10. In practice, Al reflective coatings are deposited in primary mirrors of a size up to 3.8 m in diameter in large infrared telescopes1, and those coatings have to be replaced every 2–3 years because of light scattering and reflectivity degradation resulting from scratches and corrosion. Replacing the reflectors costs extremely large amounts of time and money9. The sheer size of these enormous optical systems alone causes operational difficulties in the cleaning of the old coatings and the re-deposition of new coatings, thus making the process time-consuming and expensive9–11. Currently, achieving highly durable infrared-reflective coatings is an open and urgent challenge.

Traditionally, after the high infrared-reflective metal films such as Al, Ag and Au are deposited (step 1) (Figure 1a), transparent, hard metal oxide layers, such as SiO2 and Al2O326,27, are deposited on top (step 2) for protection, as these reflective metal films cannot withstand corrosion, scratches and other environmental damage. This route follows the typical logic of ‘achieving reflectivity first and then coating to protect’. As such, oxide films with a very high hardness28 are deposited on very soft metal films12. To avoid reflectivity loss and poor adhesion, the hard protection layer has to be very thin, usually a few dozen nanometers in thickness; thus the protection layer is often ineffective at resisting scratch damage8,10,29. Additionally, oxide films of such a thickness usually contain pinholes that undermine the protection against corrosion10. Therefore, the metal/oxide combination obtained from the traditional route is far from the ideal durability8–11,29. The traditional route also results in processing complexity because it usually involves the preparations of a variety of films to meet the multiple needs of high reflectivity, high durability and good adhesion8,10.

In this paper, we overturn the traditional ‘first reflectivity and then durability’ logic and propose a new strategy of ‘first durability and then reflectivity’ (Figure 1a). Both statements of ‘first durability and
as the cathode and the mixture of N₂ and Ar was used as the discharge gas. During the deposition, the flow rate ratios of N₂/(Ar+N₂) were increased from 3 to 100%, which was controlled by the mass flow controllers. The stoichiometry (x) of the HfNₓ films was changed from 1.039 to 1.396. The other preparation parameters were maintained constant as follows. RF power applied to the Hf target: 150 W; substrate bias: −80 V; substrate temperature: 200 °C. By varying the ratios of N₂/(Ar+N₂), we prepared HfN-only multilayer films (see Supplementary Section 7 for the parameter selections and preparation details). Additionally, we prepared Ag-doped HfNₓ films by co-sputtering the Hf and Ag target in the gas mixture of N₂ and Ar. During the deposition, the content of Ag was controlled by changing the RF power applied to the Ag target from 0 to 100 W, while the DC power applied to the Hf target was kept constant at 150 W. Other preparation parameters were kept constant as follows. Substrate bias: −160 V; substrate temperature: 200 °C; Ar flow rate: 80 sccm; N₂ flow rate: 2.8 sccm; sample rotation rate: 5 r min⁻¹. For a better comparison, an undoped HfNₓ film was also prepared under the same deposition conditions, except that the RF power of the Ag target was turned off. We prepared Al/SiO₂ films by sputtering Al and then SiO₂ target in the discharge gas of Ar. The preparation parameters were kept constant as follows. Ar flow rate: 80 sccm; DC power applied to the Al target: 60 W; RF power to the SiO₂ target: 100 W.

MATERIALS AND METHODS

Film growth

All the films were deposited simultaneously onto optical glass and single-crystal Si (001) substrates using magnetron sputtering. The work pressure of the discharge gas was maintained at 1.0 Pa for all the deposition process. Before the deposition, the glass and Si (001) substrates were successively cleaned in acetone, alcohol and deionized water using the ultrasonic cube, and then they were introduced into the vacuum chamber (base pressure of 4 × 10⁻⁴ Pa) of the sputtering system. For the preparation of HfNₓ films, a pure Hf target was chosen as the cathode and the mixture of N₂ and Ar was used as the discharge gas. During the deposition, the flow rate ratios of N₂/(Ar+N₂) were increased from 3 to 100%, which was controlled by the mass flow controllers. The stoichiometry (x) of the HfNₓ films was changed from 1.039 to 1.396. The other preparation parameters were maintained constant as follows. RF power applied to the Hf target: 150 W; substrate bias: −80 V; substrate temperature: 200 °C. By varying the ratios of N₂/(Ar+N₂), we prepared HfN-only multilayer films (see Supplementary Section 7 for the parameter selections and preparation details). Additionally, we prepared Ag-doped HfNₓ films by co-sputtering the Hf and Ag target in the gas mixture of N₂ and Ar. During the deposition, the content of Ag was controlled by changing the RF power applied to the Ag target from 0 to 100 W, while the DC power applied to the Hf target was kept constant at 150 W. Other preparation parameters were kept constant as follows. Substrate bias: −160 V; substrate temperature: 200 °C; Ar flow rate: 80 sccm; N₂ flow rate: 2.8 sccm; sample rotation rate: 5 r min⁻¹. For a better comparison, an undoped HfNₓ film was also prepared under the same deposition conditions, except that the RF power of the Ag target was turned off. We prepared Al/SiO₂ films by sputtering Al and then SiO₂ target in the discharge gas of Ar. The preparation parameters were kept constant as follows. Ar flow rate: 80 sccm; DC power applied to the Al target: 60 W; RF power to the SiO₂ target: 100 W.
RESULTS AND DISCUSSION

Optical design for achieving highly durable infrared-reflective coatings

To achieve highly durable infrared-reflective coatings, we propose a new strategy of ‘first durability and then reflectivity’ (Figure 1a), in other words, first finding a material that satisfies the durability requirement and then modifying it to obtain the required infrared reflectivity. These two steps are illustrated in detail as follows.

Step 1. Selection of a durable base. A high concentration of free electrons in a material induces a large plasma energy (Equation (1)), which in turn affects the dielectric function (Equation (2)). The relationship between the reflectivity and dielectric function can be described by Equations (2–5) Refs. 34–37.

\[ E_p = \hbar \left( \frac{4\pi n_e^2}{\varepsilon_0 m_s^*} \right)^{1/2} \]  
\[ \varepsilon(E) = \varepsilon_{\infty} - \frac{E_p^2}{E^2 - \Gamma_D^2} \]  
\[ n(E) = \frac{1}{\sqrt{2}} \sqrt{\varepsilon_1^2(E) + \varepsilon_2^2(E) + \varepsilon_1(E)} \]  
\[ k(E) = \frac{1}{\sqrt{2}} \sqrt{\varepsilon_1^2(E) + \varepsilon_2^2(E) - \varepsilon_1(E)} \]  
\[ R(E) = \frac{|n(E) - 1|^2 + k^2(E)}{|n(E) + 1|^2 + k^2(E)} \]

where the functions \( \varepsilon(E) \), \( n(E) \), \( k(E) \) and \( R(E) \) represent the complex dielectric function, refractive index, extinction coefficient and reflectance versus photon energy \( E \), respectively; the variables \( n \), \( m^* \), \( \varepsilon_0 \), \( \varepsilon_\infty \), \( E_p \) and \( \Gamma_D \) represent the concentration of free electrons, effective electron mass, vacuum permittivity, background constant, plasma energy and relaxation energy, respectively; and \( \varepsilon_1(E) \) and \( \varepsilon_2(E) \) are the real part and the imaginary part of \( \varepsilon(E) \), respectively. According to these Equations, \( \varepsilon_1^2(E) \) and \( \varepsilon_2^2(E) \) increase with \( E_p \) (Equation (2)), which induces an increase in \( n(E) \) and \( k(E) \) (Equations (3 and 4)) and a subsequent increase in \( R(E) \) (Equation (5)). The proportional relationship above between \( E_p \) and \( R(E) \) has been well demonstrated by previous simulations and experiments38. Hence, a sufficiently high concentration of free electrons is necessary for a high infrared reflectivity; metals such as Al, Ag and Au are good examples39,40. A durable material is usually associated with high hardness, which is, in essence, proportional to the degree of covalent bonding and the bond strength41. Therefore, to achieve a high durability and a high reflectivity, the ideal candidate should contain strong covalent bonds and a high concentration of free electrons. The borides, carbides and nitrides of groups IVB, VB and VIIB transition metals, hereinafter referred to as TMRs, where \( T = \text{T}, \text{Zr}, \text{Hf}, \text{V}, \text{Nb}, \text{Ta}, \text{Cr}, \text{Mo} \) and \( R = \text{B}, \text{C} \) and \( N \), have not only strong covalent bonds from the hybridization between the \( R_p \) and \( \text{TM}_d \) orbitals but also high concentrations of unbound \( d \)-orbital free electrons. The strong quasi-covalent bonds endow TMRs with a superior durability, including high bulk moduli42–44, high hardness45–47, high melting point48–50 and corrosion and abrasion resistance51–53, and makes them well known as cutting-tool coating materials54–56. The presence of unbound \( d \)-orbital free electrons causes TMRs to have similar electrical properties and infrared reflectivity characteristics to pure metals57, causing them to be widely used in the fields of optical design for achieving highly durable infrared-reflective coatings.

**RESULTS AND DISCUSSION**

**Optical design for achieving highly durable infrared-reflective coatings**

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where the functions \( \varepsilon(E) \), \( n(E) \), \( k(E) \) and \( R(E) \) represent the complex dielectric function, refractive index, extinction coefficient and reflectance versus photon energy \( E \), respectively; the variables \( n \), \( m^* \), \( \varepsilon_0 \), \( \varepsilon_\infty \), \( E_p \) and \( \Gamma_D \) represent the concentration of free electrons, effective electron mass, vacuum permittivity, background constant, plasma energy and relaxation energy, respectively; and \( \varepsilon_1(E) \) and \( \varepsilon_2(E) \) are the real part and the imaginary part of \( \varepsilon(E) \), respectively. According to these Equations, \( \varepsilon_1^2(E) \) and \( \varepsilon_2^2(E) \) increase with \( E_p \) (Equation (2)), which induces an increase in \( n(E) \) and \( k(E) \) (Equations (3 and 4)) and a subsequent increase in \( R(E) \) (Equation (5)). The proportional relationship above between \( E_p \) and \( R(E) \) has been well demonstrated by previous simulations and experiments38. Hence, a sufficiently high concentration of free electrons is necessary for a high infrared reflectivity; metals such as Al, Ag and Au are good examples39,40. A durable material is usually associated with high hardness, which is, in essence, proportional to the degree of covalent bonding and the bond strength41. Therefore, to achieve a high durability and a high reflectivity, the ideal candidate should contain strong covalent bonds and a high concentration of free electrons. The borides, carbides and nitrides of groups IVB, VB and VIIB transition metals, hereinafter referred to as TMRs, where \( T = \text{T}, \text{Zr}, \text{Hf}, \text{V}, \text{Nb}, \text{Ta}, \text{Cr}, \text{Mo} \) and \( R = \text{B}, \text{C} \) and \( N \), have not only strong covalent bonds from the hybridization between the \( R_p \) and \( \text{TM}_d \) orbitals but also high concentrations of unbound \( d \)-orbital free electrons. The strong quasi-covalent bonds endow TMRs with a superior durability, including high bulk moduli42–44, high hardness45–47, high melting point48–50 and corrosion and abrasion resistance51–53, and makes them well known as cutting-tool coating materials54–56. The presence of unbound \( d \)-orbital free electrons causes TMRs to have similar electrical properties and infrared reflectivity characteristics to pure metals57, causing them to be widely used in the fields of optical design for achieving highly durable infrared-reflective coatings.

**First-principles calculations**

The present calculations were performed by the method of projector augmented-wave pseudopotentials with density functional theory coded in the Vienna ab initio simulation package31,32. For the electrons’ exchange correlation energy, the Perdew–Burke–Ernzerhof function was used33. The kinetic energy cutoff is chosen as 550 eV for the plane wave expansion. The Brillouin zones were sampled with Monkhorst–Pack method. In order to make sure the convergence of total energy at 1 meV per atom level, the Γ-centered high-density k-point grid sets were chosen. In the calculation, we have considered the effect of spin polarization. Detailed modeling process can be seen in Supplementary Sections 3,4 and 10.

**Film characterization**

A high-resolution transmission electron microscopy (JEM-2100F, JEOL, Tokyo, Japan) and grazing-incidence X-ray diffraction measurements (D8tools, Cu Ka, Bruker, Karlsruhe, Germany) were used to characterize the structures of films. An X-ray photoelectron spectroscopy (XPS, VG ESCA LAB MKII, Thermo Fisher Scientific, Waltham, MA, USA) with a monochromatized Al Ka (1486.6 eV) X-ray source were carried out to determine the stoichiometry x, core-level spectra and valence band spectra of the HfN\(_x\) films. Before the measurement of XPS, all the samples were subjected to a 180 s Ar\(^+\) cleaning procedure to remove the surface carbon and oxygen. A Dektak surface profiler and four-point probe measurements were used to determine the thickness d and DC resistivity \( \rho \) of the films, respectively. A UV-visible spectrometer (Lambda 950, Perkin Elmer, US) was employed to obtain UV-visible reflectivity and transmission spectra, and an FTIR spectrometer (Perkin Elmer Spectrum One B type, Perkin Elmer, US) was employed to measure infrared reflectivity spectra. By analyzing the transmission spectra, we obtained the refractive indices and absorption coefficients, using a procedure reported by Swanepoel30. According to the Tauc equation, we plotted \( (a\nu)^2 \) against the photon energy \( \nu \) and calculated the optical gaps. An nanoindenter (MTS XP, MTS, US) was used to evaluate the hardness, where a continuous-stiffness-measurement mode was used. Hall-effect measurements (HL5550) were performed to obtain the concentrations of the free electrons of the films. An energy dispersive spectrometer equipped in a field-emission scanning electron microscope (SU8010, Hitachi, Tokyo, Japan) was used to determine the chemical composition of the Ag-doped HfN\(_x\) films. The corrosion behaviors of the samples were measured using an electrochemical reactor. The working electrode, reference electrode corrosion measurements, which was connected to a three-electrode configuration electron microscope (SU8010, Hitachi, Tokyo, Japan) was employed to observe the surface morphology. Before the measurement of XPS, all the samples were exposed to Ar\(^+\) etching for 30 s to remove the surface contamination. A reflection fluorescence microscopy (DM 2500M, Leica, Wetzlar, Germany) was employed to observe the surface morphology.
superconducting materials and optoelectronics. From these studies, it is known that TMRs have high durability and metal-like reflective characteristics (Figure 1b); thus TMRs are a category of ideal candidates to achieve the ultimate aim of both a high reflectivity and a high durability.

**Step II. Reflectivity enhancement.** From Figure 1b, the hardness of a TMR (14–30 GPa) is much higher than that of the reflective metals Al, Ag and Au (~0.5 GPa), but their reflectivity (40–80%) is far below that of these metals (90–98%). This explains why TMRs were basically excluded from the ‘radar screen’ in the search for infrared-reflective coatings. How to significantly increase the reflectivity of a TMR will be the key to solving the issue of needing a high durability and a high reflectivity. Taking advantage of the structural characteristics of TMRs, we propose two methods to improve the reflectivity of TMR films. One method is to deposit multilayer films on a durable TMR base to boost the reflectivity (Figure 1). These multilayer films are obtained by alternately depositing a transparent layer A and a transparent layer B of a suitable thickness on a durable TMR film, namely, TMR/A/B/.../A/B (determination of the number of layers is discussed later). According to the optical interference principle, the multilayers can achieve a very high reflectivity close to 100% in the vicinity of a target wavelength when the refractive index of layer A is far less than that of layer B, and the optical thickness nd (where n is the refractive index and d is the film thickness) of layer A and layer B both equal a quarter of the target wavelength. The other method is to introduce a metal with a high concentration of free electrons (e.g., Ag, Au) into a TMR film to form a metal–TMR alloy or a metal–TMR nanocomposite (Figure 1a). With a high concentration of free electrons, the alloys and nanocomposites are expected to have high reflectivities over the whole infrared range. Based on this principle, we incorporate gold or silver into a TMR film and explore the relationship among the composition, structure, reflectivity and durability.

**Verification experiments for achieving highly durable infrared-reflective coatings**

From Figure 1b, the near-stoichiometric HfN 

\[
\text{HfN}_{x} \quad (x = 1.039) \quad \text{and} \quad \text{HfN}_{x} \quad (x = 1.334) \quad \text{and} \quad \text{HfN}_{x} \quad (x = 1.396)
\]

nanocomposite (Figure 1a). With a high concentration of free electrons, the films are expected to have high reflectivities over the whole infrared range. Based on this principle, we incorporate gold or silver into a TMR film and explore the relationship among the composition, structure, reflectivity and durability.

**Achieving highly durable infrared-reflective coatings for a specific wavelength through multilayering.** To verify the reflectivity boost at a specific target wavelength, we develop a novel homogeneous multilayer film with three significant optical characteristics consisting entirely of HfN 

\[
\text{HfN}_{x}
\]

The creation of this multilayer originates from the unique behavior of electron localization in HfN 

\[
\text{HfN}_{x}
\]
tunable reflectivity/transmission properties. According to the measurements of the electron concentration (Figure 2a), the resistivity (Figure 2b) and the optical gap (Figure 2c), we find that, as the N/Hf ratio increases from 1:1 (a measured x value of 1.039) to 4:3 (a measured x value of 1.334), the free electrons of HfN_x films are completely localized and the films transform from a metal to a semiconductor with an optical gap of approximately 2.5 eV (see Supplementary Section 1 for more detailed discussion). Our electron concentration (Figure 2a) and resistivity measurements (Figure 2b) show that the electron localization goes through two stages of transition from slow to fast. In the first stage, the electron concentration decreases slowly from 1.46 × 10^{23} to 6.01 × 10^{20} cm^{-3} (or a decrease of <2 orders of magnitude) as x increases from 1.039 to 1.165 (over a range of 0.126 in x), and the electrical resistivity gradually increases from 110 to 636 μΩ cm (or <6 times). In the second stage, as x further increases from 1.195 to 1.334 (over a range of 0.139 in x), the electron concentration decreases sharply from 5.59 × 10^{20} to 1.67 × 10^{18} cm^{-3}, a decrease of 10 orders of magnitude. The electrical resistivity sharply increases 30 times from 1.51 × 10^3 to 4.50 × 10^4 μΩ cm. These results demonstrate that the electron localization in HfN_x films experiences two stages as x increases: x = 1.039–1.165, electrons are ‘gradually’ localized; x = 1.195–1.334, a small increase in x causes a large number of electrons to be localized, resulting in the films losing their metallic characteristic and ‘rapidly’ transform into semiconductors. The microscopic origin of the two stages is completely different. In the first stage, the formation of Hf vacancies enables partial localization of free electrons around the Fermi level and promotes new localized states from N_p, which is confirmed by a good agreement among the calculated density of states (DOS) near the Fermi level (Supplementary Fig. S3a), the distribution of electron density differences (Supplementary Fig. S3b) and the measured XPS core-level spectra (Supplementary Fig. S3c).

In the second stage, a phase transition from rock salt HfN to cubic Hf_2N_5 occurs and causes the complete localization of free electrons and the creation of new hybridized states from Hf_d and N_p. This is proven by the calculated DOS (Supplementary Figure S3d), the distribution of the electron density difference (Supplementary Fig. S3e) combined with the measured XPS valence band (Supplementary Fig. S3f) and the core-level spectra (Supplementary Fig. S3c). The Hf vacancy and phase transition in the film are identified via high-resolution transmission electron microscopy, selected area electron diffraction, Raman, X-ray diffraction and XPS (see Supplementary Section 2). All the results support each other, proving that the structures are different in the two stages. In the region of x = 1.039–1.165, the increase in x is compensated by the increasing formation of Hf vacancies, while the rock salt structure remains. In the region of x = 1.195–1.334, the further increase in x cannot be balanced by the Hf vacancies, and formation of the ε-Hf_2N_5 phase occurs. Thus, when N/Hf = 4:3 or x reaches 1.334, this phase transition is complete. Detailed discussions of the mechanisms of electron localization are given in Supplementary Sections 2-4.

Understanding the electron localization process, we explore the effect of electron localization on the optical properties of the films. We determine from the transmission spectra (Figure 2d) that before the electron localization, the HfN_x film (x = 1.039) is completely opaque, a typical metal-like characteristic, so that the transmittance of this sample is zero and there are no interference fringes. After the electron localization (x = 1.334 and 1.396), the films transform into transparent semiconductors, and thus interference fringes occur in the range of 500–2500 nm (Figure 2d). According to the Equation 2nd = mλ (ref. 2), a larger optical thickness nd (where n is the refractive index and d is the film thickness) produces more interference fringes. Therefore, the interference fringes of the film with x = 1.334 (nd = 2.78 × 625 nm) are more pronounced than those of a film with x = 1.396 (nd = 2.08 × 217 nm) due to the film’s larger refractive index and film thickness. Furthermore, the refractive index is found to decrease from 2.78 to 2.08, while the extinction coefficient remains approximately 0 (<0.001) as x increases further from 1.334 to 1.396 (Figure 2c), which is attributed to the decrease in the average molecular polarizability of the film because the polarizability of N atoms (α_N = 1.1 × 10^{-24} cm^3) (ref. 3) is much smaller than that of Hf atoms (α_Hf = 15.3 × 10^{-22} cm^3) (ref. 4). These results suggest that the optical characteristics of the HfN_x films are easily controllable by changing the stoichiometry x (Figure 2f): if x is approximately 1, the film is an opaque metal (OM); if x = 1.334–1.342, the film is a high-refractive-index transparent semiconductor (HT, n = 2.78–2.69); if x = 1.383–1.396 the film is a low-refractive-index transparent semiconductor (LT, n = 2.17–2.08).

Using this tunability of the reflectivity/transmission properties, we develop multilayers consisting of hafnium-nitride-only films: OM/(LT/HT)_n, where is the total number of repeating layers (Figure 3a and 3b). For the sake of simplicity, we refer to this structure as a ‘multilayered film’. The reflectivity of a multilayered film depends on the total number of repeating layers. According to the principle of optical interference, the more repeating layers there are (i.e., the higher the value of z), the better the reflectivity enhancement is. However, increasing the number of repeating layers increases the deposition time and the processing difficulty. Everything considered, we set the total number of repeating layers as high as 6. Thus a periodic LTHT stack with z = 6 is designed (see Supplementary Section 5). For the multilayers with δ_0 = 1.900 nm, the refractive indices of the LT and HT layers are n_L = 2.08 at x = 1.396 and n_H = 2.69 at x = 1.342, respectively. According to n_Ld_L = n_Hd_H = δ_0/4, when δ_0 = 1900 nm, the thickness of the two layers are d_L = 228 nm and d_H = 177 nm. Similarly, for δ_0 = 4100 nm, n_L = 2.17 at x = 1.383 and n_H = 2.78 at x = 1.334, d_L and d_H are 472 and 369 nm, respectively (see Supplementary Section 6 for more details). To verify the above designs, we prepare the multilayered film of OM/(LT/HT)_6 and find that the reflectivity of the OM layer improves tremendously (Figure 3c and 3d). We obtain experimentally the refractive index of each layer by controlling the composition of the films according to the relationship between the refractive index and the composition (Figure 2e). We obtain the desired thickness of each film by adjusting the deposition time. The detailed deposition parameters for the two multilayered films are given in Supplementary Tables S1 and S2 in Supplementary Information (see Supplementary Section 7). By controlling the optical thickness nd of the LT and HT layers, we achieve an infrared reflectivity higher than that of Al at a targeted wavelength δ_0. For example, when both n_Ld_L and n_Hd_H are equal to 1900/4 nm, the reflectivity of the multilayers is 99.0% at 1900 nm, exceeding that of the pure Al film (96.5% at 1900 nm) (Figure 3c). When both n_Ld_L and n_Hd_H are equal to 4100/4 nm, the reflectivity is 97.0% at 4100 nm, again higher than that of the pure Al film (96.8% at 4100 nm) (Figure 3d).

As an indication of durability, we characterize the hardness and the corrosion behavior of the multilayered film (see Supplementary Section 8). Because Al is the most commonly used infrared-reflective coating material (ref. 5), we conduct the same tests on an Al film as a comparison. The hardness of the multilayered film is 13.8 GPa, 27 times beyond that of the Al film (0.5 GPa) (Figure 3e). In a 0.5 mol L^{-1} H_2SO_4 solution, the corrosion current density of the multilayered film is 2.94 × 10^{-6} A cm^{-2}, three orders of magnitude less than that of the Al film (4.69 × 10^{-3} A cm^{-2}) (Supplementary Figure S4). In other words, the acid corrosion resistance of the
The multilayered (Supplementary Fig. S6), indicating that the corrosion resistance of multilayered HfN. Additionally, as seen in Figures 3d and 4a, the reflectance of the Ag-doped HfN (94%) at the same wavelength. This means that a multilayered HfN film has better reflective properties than an Ag-doped HfN film at a target wavelength or in a narrow band, which is very useful for many important optical applications (e.g., pointing and tracking optical systems).

Achieving highly durable infrared-reflective coatings over a range of wavelengths through silver doping. To verify the reflectivity boost over a range of wavelengths, we dope Ag into near-stoichiometric HfN film using co-sputtering. For simplicity, we refer to the Ag-doped HfN film as ‘the doped film’. We investigate the effect of the Ag content (\(C_{\text{Ag}}\)) on the structure and reflectivity. Our reflectivity measurements show that the average reflectance of the Ag-doped films in the range of 3–12 µm increases from 77 to 95% as the Ag content increases from 0 to 3.1%. However, when the Ag content further increases to 3.9%, the reflectance reduces to 80% due to an increase in the surface roughness. Additionally, it is found that the hardness of the films increases from 22.6 GPa to 25.4 GPa to 32.4 GPa as the Ag content increases from 0% to 3.1% to 3.9%. However, the hardness decreases significantly when more Ag is incorporated. Considering that the film with the Ag content of 3.1% has the highest infrared reflectivity and a relatively high hardness, we believe that the Ag doping of 3.1% is the best. Figure 4a shows the infrared reflectivity spectra of pure HfN (\(C_{\text{Hf}}=50.6\%\), \(C_{\text{N}}=49.4\%\)) and the doped film (\(C_{\text{Ag}}=3.1\%\), \(C_{\text{Hf}}=50.2\%\), \(C_{\text{N}}=46.7\%\)) together with that of an Al film as reference. The reflectivity of a pure HfN film is only 77%. In a salt solution (3.5 wt.% NaCl), the corrosion current density of the Al film is 7500 times more than that of the Ag-doped HfN multilayers, which indicate the multilayer film possesses a much higher durability than the Al film.

Multilayered film is >1500 times better than that of Al. In a salt solution (3.5 wt.% NaCl), the corrosion current density of the multilayered film is \(6.76 \times 10^{-6} \text{ A cm}^{-2}\), in contrast to that of the Al film of \(5.26 \times 10^{-2} \text{ A cm}^{-2}\) (Figure 3e and Supplementary Figure S5). This fact means the multilayered film is 7500 times more corrosion resistant than Al in this salt solution. Additionally, during salt-bath experiments (see Supplementary Section 9), the Al film shows significant corrosion after immersion in a NaCl solution at 35 °C for 5 min. When the duration time gradually increases to 180 min, the corrosion pits continue to increase (Supplementary Fig. S6). However, the multilayered film does not show any corrosion traces in the whole 10 days (14 400 min) of the salt-bath experiment (Supplementary Fig. S6), indicating that the corrosion resistance of the multilayered film in a seawater environment is easily 3000 times that of Al. These results demonstrate that the HfN_x-based multilayer film possesses a much higher scratch and corrosion resistances than pure Al. In conclusion, by exploiting the tunable properties between reflectivity and transmission induced by electron localization, we successfully achieve HfN_x-only multilayer films with both high infrared reflectivity and high durability. Compared with the conventional multilayer stacking of a variety of materials, our approach involves only one material (HfN_x) with switching of the optical states achieved by changing the stoichiometry x (i.e., via the partial pressure of nitrogen only), thus greatly simplifying the manufacturing process. Additionally, as seen in Figures 3d and 4a, the reflectance (97%) of the multilayered HfN film at 4100 nm is higher than that of the Ag-doped HfN film (94%) at the same wavelength. This means that a multilayered HfN film has better reflective properties than an Ag-doped HfN film at a target wavelength or in a narrow band, which is very useful for many important optical applications (e.g., pointing and tracking optical systems).
while that of the doped film increases abruptly to 95%, close to that of an Al film (97%) over a spectrum of 3 to 12 μm.

To explore the cause of the reflectivity enhancement, we characterize the structure of the samples. Figure 4c shows the grazing incident X-ray diffraction pattern for the pure and doped films, wherein both samples contain diffraction patterns attributed to the rock salt phase, showing that the pure and doped films have the same rock salt structure. Figure 4d shows lattice images from high-resolution transmission electron microscopy for the Ag-doped HfN film, in which well-crystallized nanograins are uniformly distributed on the film surface. The measured interplanar spacings agree well with the (111) and (200) plane spacings of the rock salt phase. These findings are consistent with the selected area electron diffraction for the Ag-doped HfN film. These results prove the formation of an Ag-doped HfN film solid solution.

Figure 4 Properties and structure of Ag-doped HfN films. (a and b) The infrared reflectivity spectra hardness and corrosion current density in a 3.5 wt.% NaCl solution for the Ag-doped HfN (930 nm), HfN (886 nm) and Al films (858 nm), where the Ag-doped HfN film has a high durability and a high infrared reflectivity. (c–e) The grazing incident X-ray diffraction pattern for the Ag-doped HfN film and HfN films c, the high-resolution transmission electron microscopy d and selected area electron diffraction e for the Ag-doped HfN film. These results prove the formation of an Ag-doped HfN film solid solution.

does not have an obvious change. This is consistent with the measured resistivity of the pure (5.4 Ω) and doped films (5.3 Ω). Additional electron states among −3.5 eV and −2 eV are introduced by the doping (Figure 5c). These extra electrons induce the charge polarization near N atoms (Figure 5b). From the band structure (Figure 5a), these extra states have a good dispersion due to the hybridization with the nearby N atoms. They have an important contribution from the free electrons to the energy of the plasma. The visible-near-infrared reflectivity spectra (Figure 5d) shows that the plasma energy of a HfN film increases significantly from 2.6 to 3.0 eV after the introduction of Ag, which agrees well with the calculation above. Previous studies have shown that the reflectivity of HfN films in the visible-infrared band depends on both the intraband transition that is related to the free electrons (described by a Drude part) and the interband transition that is related to the bound electrons (described by a Lorentz part). The reflectivity in the infrared region depends mainly on the intraband transition and is closely related to the plasma energy. The Ag-doping-induced increase in the infrared reflectivity is attributed to an increase in the plasma energy and the blueshift of the reflective cutoff wavelength (Figure 5), which expands the high-reflectivity region toward lower wavelengths.
In addition to the significant improvement of reflectivity, we find that the introduction of Ag increases the durability of the HfN film. In a 0.5 mol L⁻¹ H₂SO₄ electrolyte solution, the corrosion current density of a pure HfN film is 1.81 × 10⁻⁶ A cm⁻², whereas that of the doped film decreases to 1.14 × 10⁻⁶ A cm⁻², only 2.4% of that of the pure Al film (4.69 × 10⁻⁴ A cm⁻²) (Supplementary Fig. S8 in Supplementary Section 11). In a 3.5 wt.% NaCl electrolyte solution, the corrosion current density of the pure HfN film is 5.83 × 10⁻⁶ A cm⁻², while that of the doped film decreases to 1.90 × 10⁻⁶ A cm⁻² or only 0.04% of that of the pure Al film (5.26 × 10⁻² A cm⁻²) (Supplementary Fig. S9 in Supplementary Section 11). Additionally, the introduction of Ag causes an increase in the hardness of the HfN film from 22.6 to 25.4 GPa, or >50 times the hardness of an Al film (0.5 GPa) due to the solid-solution strengthening effect (Figure 4b). Additionally, during salt-bath experiments (see Supplementary Section 12), the doped film does not reveal any corrosion characteristics within 10 days (14 400 min), whereas the Al film shows significant corrosion pits in only 5 min (Supplementary Fig. S10), demonstrating that the doped film is much more corrosion resistant than Al in seawater. These results suggest that the Ag-doped HfN film not only has a high infrared reflectivity similar to Al but also has a much higher durability than Al. Therefore, it can be used as a highly efficient durable infrared-reflective coating.

The traditional method of improving the durability of an Al film is to deposit protective layers of oxides on its top. For example, SiO₂ (230 nm) Ref. 67, TiO₂-doped SiO₂ (180–200 nm) Ref. 9 and SiO₂/HiO₂/SiO₂ Ref. 68 films were used as the protective layers of Al films in previous studies. To compare our mirror coating with traditional ones, we deposit SiO₂ films (approximately 200 nm) on Al films using magnetron sputtering. The infrared reflectivity and hardness of these samples (Figure 6, Table 1) are consistent with the previous experimental results Ref. 67, demonstrating the reliability of our experiments. We compare the reflectivity, stability and cost of traditional mirror coating (Al/SiO₂ film) with our mirror coating (Ag-doped HfN film). The results are as follows. (1) The average reflectivities of an Ag-doped HfN film and Al/SiO₂ films are 95 and 96% at 3–12 μm, respectively (Figure 6, Table 1). This fact indicates that their infrared reflectivities are very similar. (2) According to Table 1, the acid corrosion resistance, salt corrosion resistance, wear resistance and hardness of an Ag-doped HfN film are 25 times, 53 times, 10 times and 10 times those of an Al/SiO₂ film, respectively. Additionally, the reflectivity of an Al/SiO₂ film decreases by 55% after the 10-day salt water bath test, while the reflectivity of an Ag-doped HfN film decreases by only 3%.

**Figure 5** Electronic structure of Ag-doped HfN films. (a) Band structures of Ag-doped HfN film and HfN obtained by first-principles calculations. (b) 2-D distribution of the electron density differences for an Ag-doped HfN film calculated using the formula ΔChg (x) = ChgAg-doped HfN film (x) - ChgHfN/VHf (x) - ChgAg (x), where ChgAg-doped HfN film (x), ChgHfN/VHf (x) and ChgAg (x) are the real space distributions of the charge densities of an Ag-doped HfN film, HfN with the Hf vacancy (V_Hf) and an Ag atom. (c) DOS and partial DOS (PDOS) of an Ag-doped HfN film and HfN. (d) The UV-visible reflectivity spectra for the Ag-doped HfN film and HfN films, which indicate that the plasma energy of the two samples are 3.0 and 2.6 eV, respectively. These results show that the enhancement of the reflectivity is attributed to the increase of the plasma energy.
These results show that Ag-doped HfN films have much higher durabilities and stabilities of the reflectivity than Al/SiO2 films. (3) In our sputtering experiments, an Al target (diameter 60 × 3 mm) costs approximately 25 dollars, a SiO2 target (diameter 60 × 3 mm) costs approximately 50 dollars, a Hf target (diameter 60 × 3 mm) costs approximately 290 dollars and an Ag target (diameter 60 × 3 mm) costs approximately 150 dollars. Therefore, taking the cost of the raw materials into account, the Ag-doped HfN film is more expensive than the Al/SiO2 film. However, the Ag-doped HfN film only needs to deposit a one-layer film, which is easier than the two-step preparation of the two-layer Al/SiO2 film. Moreover, the Ag-doped HfN films have much higher durabilities and stabilities. Thus we believe that the cost of the two mirror coatings is very similar. These results suggest that the Al/SiO2 films have slightly better reflectivities and a lower cost than the Ag-doped HfN films, but their durabilities and stabilities of the reflectivity are far lower than those of Ag-doped HfN films. Thus the traditional mirror coating is more suitable for moderate environments, while our mirror coating obtained by the new strategy is more suitable for harsh environments, such as those with dust, windblown sand, moisture, acid rain and salt fog.

**Table 1 Stability of reflectivity, hardness, wear rate and corrosion current for Ag-doped HfN and Al/SiO2 films**

| Ag-doped | HfN | Al/SiO2 | Comparison |
|----------|-----|--------|------------|
| Reflectance (3–12 μm) | 95% | 96% | 1% lower than Al/SiO2 |
| As-deposited | 92% | 41% | 51% higher than Al/SiO2 |
| After immersion in a NaCl solution at 35 °C for 10 days | | | |
| Hardness (GPa) | 25.4 | 2.5 | 10:1 (10 times) |
| Wear rate (10−5 mm³ N−1 m−1) | 1.03 | 11.76 | 1:10 (10 times) |
| Corrosion current (A cm−2) | | | |
| 0.5 mol l−1 H2SO4 | 1.14E-05 | 2.90E-04 | 1:25 (25 times) |
| 3.5 wt.% NaCl | 1.90E-06 | 1.02E-04 | 1:53 (53 times) |

**CONCLUSIONS**

We propose an alternative design approach of ‘first durability and then reflectivity’ to achieve the goal of both high durability and reflectivity.

**Figure 6** (a) The reflectance spectra of the Ag-doped HfN films before/after immersion in a NaCl solution at 35 °C for 10 days. (b) and (c) Surface of these Ag-doped HfN films before immersion (0 day) and after immersion for 10 days. (d) The reflectance spectra of Al/SiO2 film before/after immersion in the same NaCl solution for 10 days. (e) Reflectance of the Al/SiO2 films at various infrared wavelengths (2, 2.5, 4 and 10 μm) as a function of the immersion time. (f-i) Typical surface of Al/SiO2 films before immersion (0 day), after immersion for 4 days, 5 days and 10 days.
We recommend transition metal compounds, TMR (TM = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W; R = B, C, N), as the durable base material and then improve its reflectivity to achieve the integration of high durability and reflectivity. The two validation experiments on HfN prove that our new strategy and approaches work as expected. The coatings thus obtained not only have an infrared reflectivity performance close to that of aluminum but also have a far better durability. The traditional mirror coating (e.g., Al/SiO$_2$ films) is more suitable for moderate environments, while our mirror coating that is obtained by the new strategy (e.g., Ag-doped HfN film) is more suitable for harsh environments, such as those with dust, windblown sand, moisture, acid rain and salt fog. This research opens up whole new areas in developing durable infrared-reflective coatings. HfN is only 1 of the 27 TMR transition metal compounds; thus this study can be considered one point in the whole spectrum of possibilities, that is, zero TMR transition metal compounds; thus this study can be considered developing durable infrared-re.

Furthermore, the inherent properties of each TMR can be improved by modulating its structure (multilayering, alloying, nano-compositing, etc.); thus new three-dimensional studies may emerge in this area. As such, new materials, new functions and new mechanisms are expected to be developed. This study has ushered the transition metal compounds from hard protective coatings (e.g., cutting-tool coatings) into a completely new area of optical coatings. This rejuvenates the study of the transition metal compounds.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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