Microstructure and Photothermal Conversion Performance of Ti/(Mo-TiAlN)/(Mo-TiAlON)/Al₂O₃ Selective Absorbing Film for Non-Vacuum High-Temperature Applications

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Abstract: This paper aims to clarify the phase composition in each sub-layer of tandem absorber TiMoAlON film and verify its thermal stability. The deposited multilayer Ti/(Mo-TiAlN)/(Mo-TiAlON)/Al₂O₃ films include an infrared reflectance layer, light interference absorptive layers with different metal doping amounts, and an anti-reflectance layer. The layer thicknesses of Ti, Mo-TiAlN, Mo-TiAlON, and Al₂O₃ are 100, 300, 200, and 80 nm, respectively. Al content increases to 12 at.% and the ratio of N/O is nearly 0.1, which means nitride continuously changes to oxide. According to X-ray Diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) results, the diffraction peak that appears at 2θ = 40° demonstrates that Mo element aggregates in the substitutional solid solution (Ti,Al)(O,N) columnar grain. TiMoAlON films have low reflectivity in the spectrum range of 300–900 nm. When Al content is more than 10 at.%, absorptivity is almost in the spectrum range from visible to infrared, but absorptivity decreases in the ultraviolet spectrum range. When Al content is increased to 12 at.%, absorptivity α decreases by 0.05 in the experimental conditions. After baking in atmosphere at 500 °C for 8 h, the film has the highest absorptivity when doped with 2 at.% Mo. In the visible-light range, α = 0.97, and in the whole ultraviolet-visible-light near-infrared spectrum range, α = 0.94, and emissivity ε = 0.02 at room temperature and ε = 0.10 at 500 °C.

Keywords: TiMoAlON film; dual gas reactive sputtering; plasma emission monitor; selective absorbing; photothermal application

1. Introduction

Renewable energy has gained more and more attention for the depletion of fossil fuels, green-house gases, and climate changes. Solar energy is one of the most abundant and environmentally friendly energy sources, and photothermal conversion is the most simple and convenient method to be utilized [1]. Because of commercial energy storage systems, fledged grid technology, and equipment, solar thermal power generation is considered to be a most promising method for basic electricity supply. Parabolic trough concentrating solar power is an established suitable technology for large-scale commercial application [2], but of which, the concentrating solar collector usually requires high-cost accessories, such as high-temperature-resistant coating, high-vacuum glass tubes, metal pipes, and vacuum sealing. Besides that, solar vacuum tubes also have high maintenance costs. In view of this, there is an urgent need to design and develop a concentrating solar collector that can be exposed in atmosphere environment at high temperatures without the vacuum tube’s protection. So, selective absorbing film with excellent high-temperature oxidation resistance and thermal stability is of great concern.

A gradual multi-layer structure is usually designed to meet the requirements of high-temperature oxidation resistance and thermal stability. Metal nitrides [3] or carbides [4] have been proven to be effective for high absorptance in the solar spectrum region of...
0.3–2.5 μm and low thermal emittance in the infrared region of 2.5–25 μm, but they require an outer vacuum glass chamber, or intrinsic absorption will become weakened during the slow oxidation process. To work in air at high temperatures, an oxygen atom is added to the film surface layer to defer oxidation reaction. This film structure has a good effect at first, but for a long time the absorptivity will become lower due to internal diffusion and chemical component homogenization of the oxygen (O) atom. Life span becomes a noticeable problem for non-vacuum high-temperature application, and how to offset the reduction of intrinsic absorption is a pressing problem.

Multicomponent TiMoAlON film with Ti/(Mo-TiAlN)/(Mo-TiAlON)/Al2O3 multilayer structure is designed for non-vacuum high temperatures. TiMoAlON photothermal films take (Ti,Al)N and (Ti,Al)(O,N) compounds as an absorbing dielectrics layer, and Mo as a doping element to form a metal ceramic composite layer after O atom internal diffusion. So, the main absorber layer can gradually change from a dielectric layer to a metal-ceramic composite layer. With multiple absorption mechanisms, intrinsic absorption film [5] and cermet film [6] are performed separately or jointly throughout the whole life span. Al is selected as a doping element because of its high chemical affinity to the O atom. Ultrafine Al particles embedded into the film can increase the consumption of the internal-diffused O atom, so as to improve oxidation resistance at high temperatures. In addition, Al doping into the TiN substrate can form an impurity energy level in the TiN bandgap, which can increase intrinsic absorption in the visible spectrum. Mo doping into (Ti,Al)(O,N) substrate can improve light absorption because of inter-band optical transitions and resonance absorption. To obtain high absorptance and low thermal emittance at high operating temperatures, it is essential to ensure an absorber-reflector tandem [7], so it requires to form a multi-layer structure within the micro-nano scale. In such a film structure, the absorber is used to provide high absorptance in the solar spectrum region, while the reflector is designed to provide high reflectance in the thermal infrared region. Therefore, the solar absorber coating, according to this idea, generally has a multi-layer structure, as shown in Figure 1. Based on the multi-layer structure, an interference effect can be designed to promote TiMoAlON films’ absorptivity [8].

![Cross-sectional schematic of graded-index TiMoAlON photothermal film](image)

**Figure 1.** Cross-sectional schematic of graded-index TiMoAlON photothermal film [8].

Gradually varied bimetallic nitride, bimetallic oxynitride, and metallic oxide are important for photothermal conversion. The stoichiometric ratio of each compound decides the final properties. The reactive sputtering process tends to be highly unstable. Commonly, with the increased flow of reactive gases (i.e., N2 and/or O2), there is a sudden drop
of sputter yield due to the target surface becoming fully covered by reaction products. Generally, a high-rate reactive deposition process should be operated between metallic state and nonconductive ceramics [9]. To work successfully in such a quick dropped transition region, a rapid reactive gas control system is required. PEM (plasma emission monitor) is the most commonly adopted method and can also be used in combination with other techniques if required [10,11]. Besides that, to precisely control metal nitrides’ gradual change to oxy-nitrides and oxides (i.e., (Ti,Al)N, (Ti,Al)(NO), Al2O3) is an arduous task. So, a N2–O2 dual-gas reactive direct current magnetron sputtering (dcMS) system is used to control the depositing process based on the developed plasma emission spectrum monitoring (PEM) feedback adjusting system [8].

The setup of the N2–O2 dual-gas reactive dcMS system is shown in Figure 2: light is guided to the monochromator through a light guide. Then, the characteristic atomic emission spectrum line is monitored by a monochromator, the intensity of which at a specific wavelength is inversely proportional to the target poisoning. Then, a piezo-electric valve can rapidly adjust the gas flow by regulating the piezo valve state, so as to maintain the transitional state. The detailed setup is elaborated in Reference [8]. Considering the feedback controlling mechanism of the PEM controller for depositing nitrides/oxides, a ‘cheating’ control mode is proposed to deposit oxy-nitrides by using dual reactive gases (i.e., N2–O2). As shown in Figure 2, an auxiliary gas pipeline for O2 flow, which is controlled by a MFC (mass flowmeter controller), was added to the system. When the vacuum chamber is supplied with auxiliary O2, it will also cause the additional characteristic spectral line intensity reduction. However, for the PEM-controlled nitrogen supply system, it seems to produce a feedback result of nitrogen overdosing. Then, the PEM controller will reduce N2 supply according to the given set point. This method can gradually change nitrides to oxides.

![Figure 2. Schematic diagram of the setup of the plasma emission monitor (PEM)-controlled dual-gas reactive direct current magnetron sputtering (dcMS) system [8].](image)

In view of this, it is necessary to obtain a multi-layer tandem absorber which has fine inter-layer diffusion resistance, and precise control of the O/N ratio in oxy-nitrides layers. In order to prepare constituent TiAlON coatings with smoothly and precisely controlled O/N ratio, the PEM-controlled N2–O2 dual-gas reactive DC magnetron sputtering method is applied. To evaluate the thermal stability of the films, they are all baked for certain duration in atmospheric environment at high temperatures. In this paper, the effect of various process parameters on the layer structures and phase constitution of TiMoAlON selective absorbing films are discussed to clarify the photothermal properties.

2. Experimental Details

The closed-field unbalanced magnetron sputtering system MSIP-016 with Ti, Al, and Mo targets was used for the experiments, as shown in Figure 3. SiO2 and monocrystalline
silicon substrates were used for deposition. TiMoAlON film on SiO$_2$ substrate was used for the transmittance and reflectance test and the film on monocrystalline silicon substrate was used for elements and phase composition analysis. The reactive magnetron sputtering was controlled with the modified PEM controller, as mentioned before [8]. The substrate bias voltage was $-45$ V and the main axle rotating speed of the samples’ holder was 5 rpm. N$_2$ was supplied by the PEM controller and O$_2$ was supplied by MFC. A Ti atomic emission spectrum line intensity of 501 nm was monitored by PEM to control the N$_2$ supply.

Before depositing, the samples were chemically cleaned by ultrasonic in acetone and absolute alcohol solution for ten minutes, respectively. The vacuum chamber was pumped down to a base pressure of $4.0 \times 10^{-3}$ Pa, and then the targets were cleaned in situ by argon ion bombardment for 15 min, wherein a DC bias of $-400$ V was applied. The detailed preparation parameters are described in Table 1. In addition, it is an arduous task to deposit Al$_2$O$_3$ film using DC reactive magnetron sputtering, so the processing parameters of preparing stoichiometric Al$_2$O$_3$ must be obtained in advance by the PEM-monitored plasma emission spectrum intensity of Al. Simultaneously, the vacuum chamber was inflated with oxygen, the flow rate of which is gradually and slowly increased until the Al target is ‘poisoned’, and it reaches the maximum current of the Al target. The deposited films were baked at 500 °C in atmosphere for 8 h to investigate their thermal stability. A JSM-6700F field emission scanning electron microscope was used for cross-section morphology observation. Oxford energy dispersive spectroscopy was used for composition analyses. A Shimadzu X-ray diffractometer was used to analyze phase structures, the scanning model of which is grazing incidence, and the grazing incident angle was 2°, the scanning area was 20–80°, and the scanning speed was 10°/min. A JEOL JEM-3010 transmission electron microscope was used for the fine-layer structure analysis. A Hitachi U-4100 spectrophotometer was used for transmissivity and reflectivity observation. The test value of reflectivity is the intensity ratio of reflected light and incident light. The absorptivity in the spectral region 300–2400 nm is an integral value. The integral value is approximated by subsection summation according to the following equation. During the calculation, the tested spectrum is equally divided into 50 sections.

$$\rho_s = \frac{\sum_{i=1}^{n} \rho_{\lambda i} E_s(\lambda_i) \Delta \lambda_i}{\sum_{i=1}^{n} E_s(\lambda_i) \Delta \lambda_i}$$

where, $\rho_s$ is the reflectivity in the tested spectrum range, $\rho_{\lambda i}$ is the tested reflectivity value when light wavelength is $\lambda_i$, and $E_s(\lambda_i)$ is the light intensity when the light wavelength is $\lambda_i$. A modified Fourier transform infrared spectrometer was used for emissivity measurement. The wavelength domain for the emissivity was 5–20 µm.
Table 1. Process parameters for depositing Ti/Mo-TiAlN/Mo-TiAlON/Al$_2$O$_3$ film.

| Sub-layer                        | Duration/s | Ion Current of Targets/A | PEM Set-Point/% | O$_2$ Flow Rate/Sccm |
|----------------------------------|------------|--------------------------|-----------------|----------------------|
| infrared layer (Ti)              | 300        | Mo: 0, Al: 0, Ti: 4.0    | 100             | 0                    |
| main absorber (Mo-TiAlN)         | 900        | Mo: 0, Al: 1.0, Ti: 0–0.6/0.9/1.2 | 50, 0.9, 0      |
| secondary absorber (Mo-TiAlON)   | 360        | Mo: 0.6/1.0/1.2–0, Al: 0.9, Ti: 0.2 | 50, 0–8.5      |
| antireflective layer (Al$_2$O$_3$)| 180        | Mo: 0, Al: 0, Ti: 3.0 | OFF             | 8.5                  |

3. Results and Discussion

3.1. Composition and Phase Analysis of the Film

It has been reported that the absorptivity of single-layer TiAlN film is about 0.8 [12], and TiAlON film has low reflectivity (below 16%) and high absorptivity in the visible-ultraviolet spectrum. Photothermal conversion performance of titanium nitride coatings can be tailored by controlling the stoichiometric ratio of Ti and N, which affects the free electrons density of the Ti d-band [13]. So, the overall proportion of N and O elements, that is compounds in the film, play a key role in determining the performance of photothermal conversion.

Depositing the TiMoAlION film controlled by the N$_2$–O$_2$ dual-gas reactive sputtering system, the ratio of N/O is varied adaptively with sputtering yield of Al (or Ti), so by changing the target current of Al (or Ti), different metallic compounds are finally obtained. Doping N or O elements in TiN$_x$ matrix can change the electronic band structure. When the proportion of O atoms comes up to a certain ratio in TiON matrix, the nitride dielectric layer will turn into oxide. For that, each kind of compound (nitride, oxide) has a different absorption edge, and if any nonstoichiometric compounds can be regulated and deposited, an absorption plateau will appear in the absorption curve.

In view of the above, Al content is set as variable to deposit the film. The ratio of N/O changes with Al content, as shown in Figure 4. Increased Al target current tends to form metallic oxide. Al content increases to 12 at.%, and the ratio of N/O is nearly 0.1. Nitride is continuously changed to oxide. The Al atom can capture the O atom to establish a new equilibrium point for the feedback system. So, different proportions of nitride and oxide in each sub-layer can be achieved; accordingly, the refractive index (n) and extinction coefficient (k) of the whole film can be changed gradually due to the type of gradient material (nitride, oxynitride, oxide) [13]. The refractive index decreases from the bottom to the surface. Doping O, N, and Al elements into TiN$_x$ matrix, the k value is continuously adjusted; that is, absorption peaks will shift towards short wave with the increase in doping elements. So, overlapped impurity energy level can broaden the absorption peak.

Figure 4. Effect of target current on Al content and the ratio of N/O.
The film is designed to use in non-vacuum and high-temperature environment, and slow oxidation at high temperatures is inevitable. Besides that, the oxygen atom will diffuse among each sub-layer. For long-time application, composition homogenization will narrow the intrinsic absorption limit. So, doping Mo element in the film to form a ceramic-metal composite can offset the absorption reduction caused by oxidation. As seen in Figure 4, as Mo content increases in the film, the ratio of metallic elements (Ti, Al) and non-metallic elements (N, O) changes slightly, as shown in Figure 5. That implies that Mo does not participate in the reactive sputtering process. They possibly exist in each layer in the form of metal Mo, as demonstrated by XRD results. Figure 6 shows phase constitution variation with the increase of Mo content. A weak diffraction peak appears at $2\theta = 40^\circ$ when doping Mo into the film occurs. Referring to PDF standard cards, it is supposed to be a diffraction peak of the Mo (110) crystal face. The diffraction peak intensity increases with Mo content. So, metal Mo exists in the film and its proportion increases with target current. In the case of a 1% small Mo peak, the diffraction angle is $38^\circ$, which is in close proximity to the diffraction peak of TiN(111) or TiO(111). Considering that the diffraction peak intensity of $2\theta = 36^\circ$ is lower than other samples, it implies that TiN or TiO grain size is small and compounds content is low. That may be caused by Ti(N, O) compounds’ decrease because Ti is substituted by Al, and forms (Ti, Al)(N, O) substitutional solid solution. Al atomic radius is smaller than the Ti atom. Interplanar spacing of (Ti, Al)(N, O) is smaller than TiN or TiO, so the diffraction peak shifts to a larger angle and a small diffraction peak appears at $2\theta = 38^\circ$. (Ti, Al)(N, O) substitutional solid solution is speculated to form the diffraction peak at $2\theta = 38^\circ$, and Ti(N, O) and Al(N, O) are possible matrices of the as-deposited film. They perform different intrinsic absorbing functions, including doping elements.

![Graph](image1.png)

**Figure 5.** Effect of target current on Mo content and ratio of (Ti + Al)/(N + O).

![Graph](image2.png)

**Figure 6.** Effect of Mo content on phase constitution of TiMoAlON films.
3.2. Microstructure Characterization

The surface SEM images of Ti/(Mo-TiAlN)/(Mo-TiAlON)/Al₂O₃ films before and after baking are shown in Figure 7. The film surface is coarse in Figure 7a. After baking at 500 °C in atmosphere for 8 h, unreacted Al is oxidized and the surface Al₂O₃ layer becomes more pure. The surface layer becomes fine and compact, as seen in Figure 7b.

![Figure 7. Surface SEM images of TiMoAlON film (a) before and (b) after baking.](image)

The cross-sectional SEM image of the Ti/(Mo-TiAlN)/(Mo-TiAlON)/Al₂O₃ tandem absorber is shown in Figure 8. An obvious multi-layer structure that matches the theoretical design (as seen in Figure 1) is obtained, which indicates that the PEM-controlled reactive sputtering method is feasible to deposit the multi-layer compound film within the nanoscale. It clearly shows that the tandem absorber consists of four sub-layers. Above the substrate, the complex films include an infrared reflectance layer, interference absorptive layers with different metal volume ratios, and an anti-reflectance layer. The layer thicknesses of Ti, Mo-TiAlN, Mo-TiAlON, and Al₂O₃ were found to be approximately 100, 300, 200, and 80 nm, respectively. A compact Al₂O₃ layer is coated on the surface, which act as an antireflective layer and diffusion barrier of O atoms.

![Figure 8. Cross-sectional morphology of TiMoAlON selective absorbing films.](image)
Figure 9 shows TEM images of TiMoAlON film. Above the infrared reflectance layer (Ti layer), there are distinct columnar grains in the tandem absorber layers. Doping with Mo element, there are many dark accumulations aggregating in the columnar crystal, as shown in Figure 9b, the \( d \) value of which, calculated from HRTEM data in Figure 9c, is 0.2185 nm. It is a close match with body-centered cubic Mo(110), and its grain size is 3–5 nm, statistically. Mo nanocrystalline tends to aggregate in the center of TiN grain, and an undoped region exists between two neighboring columnar crystals, as seen in Figure 9c. This structure can form a light trap for certain wavelengths of light, and multiple reflections between Mo aggregating zones extend the optical travelling path and enhance the absorption.

![TEM images of TiMoAlON selective absorbing films](image_url)

**Figure 9.** TEM images of TiMoAlON selective absorbing films. (a) Cross-sectional microscope, (b) HRTEM image of columnar grain, (c) HRTEM image of the zone between two neighboring columnar crystals, and (d) SAED pattern of zone A.

In columnar crystals, lattice fringes spacing is 0.1483 nm, which is a pretty good match with TiO\(_2\) (200). Because \( d \) values of TiAIN and TiAlON are close to TiN, it is difficult to differentiate the dielectric materials, but substitution of solid solution (Ti,Al)(N,O) compound is quite possible. The selected area diffraction pattern of zone A in Figure 9d shows a spotty ring pattern, and some rings are undistinguished because TiN(220) and Mo(200), TiO(200), and Mo(110) have similar \( d \) values, respectively.

When Mo content is less than 3 at.\%, they do not aggregate, as mentioned before, instead, they form a nano-scale multilayer film. Metal Mo is interspersed in the Ti(Al,N) and (Ti,Al)(N,O) compounds matrix. From the bottom up, they are gradually decreased, as seen in Figure 10. Above zone C, oxides act as the main matrix materials. The gradient structure is obvious: it can fulfill photothermal conversion when exposed to light, which goes through the film in a top-down approach, just like a process of light filtration. Although increasing Mo content does not form a columnar structure in the dielectric matrix, the multi-layer structures also present a high absorption property due to continuous reflection among the neighboring layers.
3.3. Photothermal Conversion Performance

According to the definition of absorbance ($\alpha$), transmittance ($\tau$), and reflectance ($\rho$), it is known that $\alpha + \tau + \rho = 1$. Because the infrared reflected layer is opaque, consequently, $\tau \approx 0$, and the absorptance $\alpha = 1 - \rho$. The photothermal conversion property ($\alpha$, absorbance, and $\varepsilon$, emissivity) was observed using an ultraviolet-visible-near-infrared spectrophotometer and emissometer. Figure 11 shows the effect of Al content on reflectivity of TiMoAlON film, which confirms the above analysis that the ratio of oxide and nitride has an effect on solar spectrum absorptivity.

![Cross-sectional TEM image of TiMoAlON film with Mo content of 3 at%](image)

**Figure 10.** Cross-sectional TEM image of TiMoAlON film with Mo content of 3 at%.

![Reflectivity vs. Wavelength graph](image)

**Figure 11.** Effect of Al content on reflectivity of TiMoAlON selective absorbing films.

TiMoAlON film has low reflectivity in the spectrum range of 300–900 nm, then it increases sharply in the near-infrared spectrum range, as seen in Figure 11. According to Kirchhoff’s law of thermal radiation, high reflectivity in the infrared region demonstrates a relatively low heat radiation when it serves at high temperature. Absorptivity in the visible spectrum increases with Al content, but when its content is over 10 at.%, absorptivity is similar in the range from visible to infrared. The difference is just in the ultraviolet...
spectrum. When Al content is increased to 12 at.%, absorptivity decreases by 0.05 in the ultraviolet spectrum range. Al doping in TiN matrix can change its bond structure (e.g., TiN to (Ti,Al)N and (Ti,Al)(ON)) [14,15], so absorptivity is varied accordingly to different matrix materials, but the superfluous Al atom does not take part in the reactive sputtering process. Considering the higher reflectivity in the UV spectrum region, TiMoAlON film with Al content of 10 at.% can achieve the highest absorptivity.

To serve in non-vacuum environment at high temperatures, the as-deposited films were baked in atmosphere at 500 °C for 8 h to evaluate their thermal stability. Figure 12 shows reflectivity variation with Mo content after thermal oxidation in atmosphere at 500 °C for 8 h. Under the experimental conditions, 10 at.% Al is the optimum doping amount. Absorptivity has little change after thermal oxidation, which is consistent with Barshilia’s conclusion about thermal stability of TiAlN/TiAlON/Si3N4 tandem absorbers prepared using direct current magnetron sputtering [16–18]. It has high absorptivity, α = 0.94, and low emissivity, ε = 0.02 at room temperature and ε = 0.10 at 500 °C. The as-deposited films doped with Mo do not improve absorptivity at the early stage because of strong intrinsic absorption, but surface plasma resonance absorption caused by the embedded ultra-fine Mo in oxide ceramic matrix will take effect after thermal oxidation, which offsets the intrinsic absorption reduction.

When doped with 2 at.% Mo, film has the highest absorptivity, absorptivity of which in the visible-light range almost reached 0.97. When Mo content is below 2 at.%, optical absorption becomes weaker with lower Mo atomic percent. When Mo content was increased to 3 at.%, Mo particles aggregated and formed a multilayer structure, which remarkably decreased Mo specific area. After thermal oxidation, absorptivity in the visible spectrum becomes lower.

4. Conclusions

With the help of the N2-O2 dual-gas reactive sputtering system, Ti/(Mo-TiAIN)/(Mo-TiAlON)/Al2O3 tandem absorbing films were deposited, matching the theoretical design. The complex films include an infrared reflectance layer, interference absorptive layers with different metal doping amounts, and an anti-reflectance layer. The layer thicknesses of Ti, Mo-TiAIN, Mo-TiAlON, and Al2O3 were found to be approximately 100, 300, 200 and 80 nm, respectively.
When Al target current was increased, it tended to form metallic oxide. With an increase of Al content to 12 at.%, the ratio of N/O was nearly 0.1. Nitride is continuously changed to oxide. When Mo content was increased in the film, the ratio of metallic elements (Ti,Al) and non-metallic elements (N,O) changed slightly. XRD and HRTEM results showed that a diffraction peak appears at $2\theta = 40^\circ$, demonstrating that Mo element aggregates in substitutional solid solution (Ti,Al)(O,N) columnar grain in the form of metal Mo.

TiMoAlON films have low reflectivity in the spectrum range of 300–900 nm, and they increase sharply in the near-infrared spectrum range. Absorptivity in the visible spectrum increases with Al content. When Al content was more than 10 at.%, absorptivity was almost in the spectrum range from visible to infrared, but absorptivity decreased in the ultraviolet spectrum range. When Al content was increased to 12 at.%, absorptivity, $\alpha$, decrease by 0.05 in the experimental conditions. After baking in atmosphere at 500 °C for 8 h, the film had the highest absorptivity when doped with 2 at.% Mo. In the visible-light range, $\alpha = 0.97$, and in the whole ultraviolet-visible-light near-infrared spectrum range, $\alpha = 0.94$, and emissivity ($\varepsilon$) = 0.02 at room temperature and $\varepsilon = 0.10$ at 500 °C.

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