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## PAPER

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#### Introduction 1.

Vanadium dioxide  $(VO_2)$  is the best thermochromic material for energy-efficient smart windows.<sup>1,2</sup> At the critical temperature  $(\sim 68 \,^{\circ}\text{C})$ , a reversible semiconductor-to-metal transition occurs in bulk VO2.3 Accompanied with the crystal structure transitioning from rutile phase (R) to monoclinic phase (M),  $VO_2$ exhibits a drastic change in electrical conductivity and NIR optical transmittance.<sup>4</sup> Such specific features make VO<sub>2</sub> a potential candidate in the application of thermochromic energy-efficient smart windows, uncooled infrared (IR) microbolometers, laser protection and optical storage devices.5-8 High-purity VO<sub>2</sub> films can be fabricated by many preparation methods, including the pulsed laser deposition, sol-gel method, chemical vapor deposition (CVD), thermal

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Enhanced visible transmittance and reduced transition temperature for VO<sub>2</sub> thin films modulated by index-tunable SiO<sub>2</sub> anti-reflection coatings

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The low visible transmission is one of the bottleneck problems for the application of vanadium dioxide films since the high refractive index (RI) of  $VO_2$  films results in strong reflection in the visible wavelength. To address this problem, in this paper, high-purity VO2 films were deposited on fused silica by DC reactive magnetron sputtering at low temperature of 320 °C. Silica sol-gel coatings with tunable refractive index (RI) coated onto VO<sub>2</sub> films have been fabricated to enhance visible transmittance with the potential application in the field of smart windows. SiO<sub>2</sub> coatings with tunable RI (1.16–1.42 at  $\lambda = 700$  nm) were prepared by sol-gel dip-coating technique. The double structure SiO<sub>2</sub>/VO<sub>2</sub> films were characterized through several techniques, including X-ray diffraction, UV-VIS-NIR spectrophotometry and scanning electron microscopy. Compared with the single-layer VO<sub>2</sub> film ( $\Delta T_{sol}$  of 6.25% and  $T_{lum}$  of 38.58%), the three kinds of SiO<sub>2</sub>/VO<sub>2</sub> bilayer films had higher  $T_{lum}$  (41.93–50.44%) and larger  $\Delta T_{sol}$  (8.15–8.51%) simultaneously due to significantly decreased reflectance. Moreover, the crystallization properties of VO<sub>2</sub> films are essentially unchanged by applying a SiO<sub>2</sub> top layer, while the phase transition temperature and thermal hysteresis width of sample S116 are lower than those of pure VO<sub>2</sub> film. The presented RI-tunable SiO<sub>2</sub> coatings, can regulate optical properties continuously for various VO<sub>2</sub> substrates, paving the way for practical applications of VO<sub>2</sub> films in the field of smart windows or others.

> evaporation, atomic layer deposition and magnetron sputtering.9-14 Among these, magnetron sputtering technology shows great advantages for the application of VO<sub>2</sub> films in smart windows due to the good uniformity and potential for industrialization.15

> Up till now, there has been no successful application of vanadium dioxide in the field of smart windows. To realize an available solution, several challenges needed to be overcame: low solar modulating ability, unattractive color, high transition temperature and especially low visible transmittance. Generally, the low transmission of single 80 nm VO<sub>2</sub> film can only reach 40% in the visible region (380-780 nm).16 There have been various popular methods to enhance the visible transmittance of VO2 films: metal-ion doping,17 multilayer structure,18 porous texture,<sup>19</sup> etc. Moreover, VO<sub>2</sub> films with different nanostructures can behaver enhanced  $T_{lum}$  and  $\Delta T_{sol}$ , such as moth eye structure,<sup>20</sup> photonic structure,<sup>21</sup> plasmonic structure<sup>22</sup> and grided structure23. Additionally, applying antireflection coatings (ARCs) on the film surface can also be a promising approach to improve the visible transmittance of VO<sub>2</sub> films through TiO<sub>2</sub>, ZnO, ZrO<sub>2</sub> or SiO<sub>2</sub>, etc.,<sup>24</sup> which is useful in industrial applications. The anti-reflective devise of double-layer films should be enhanced as the high RI and reflectivity of VO2 films in the

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visible region. However, most of the overcoats are usually with high RI, expensive and energy-consuming. It is worth noting that compared with other antireflection coatings, the SiO<sub>2</sub> coatings with low RI prepared by low-cost sol-gel methods behaved some advantages of large-area, widespread used and anti-oxidation.<sup>25,26</sup> Much research has been devoted to the fabrication of SiO<sub>2</sub>/VO<sub>2</sub> double-layer structure to improve the visible transmission of VO<sub>2</sub> films significantly. Yu *et al.* increased the  $T_{lum}$  of VO<sub>2</sub> film from 37.6% to 47.7% *via* SiO<sub>2</sub>/ VO<sub>2</sub> composite structure, while  $\Delta T_{sol}$  exhibited an obvious decrease trend from 8.06% to 7.62%.<sup>27</sup> Zhang *et al.* introduced SiO<sub>2</sub> with RI of 1.299 as an antireflection coating coated on the VO<sub>2</sub> film, which improved the visible transmission from 69.8% to 80.0% significantly, whereas the NIR control capability was also slightly decreased from 12.6% to 10.2%.<sup>28</sup>

Therefore, in this study, SiO<sub>2</sub> anti-reflection coatings with tunable refraction index were coated on VO<sub>2</sub> films to enhance  $\Delta T_{sol}$  and  $T_{lum}$  simultaneously and continuously. Furthermore, the RI tunability of top SiO<sub>2</sub> coatings can be applied to not only the VO<sub>2</sub> continuous thin films but also the nanocomposites and micro-patterned VO<sub>2</sub> films to improve the nanothermochromism effect.<sup>29</sup> In addition, an anti-oxidation overcoat is also necessary for the unstable VO<sub>2</sub> films. Index-tunable anti-reflection SiO<sub>2</sub> coatings optimized by sol–gel method prepared on the surface of  $VO_2$  films by sol-gel dip-coating technique. The effect of RI tunability of  $SiO_2$  coatings on the thermochromism and optical properties of  $VO_2$  films was investigated.

## 2. Experimental details

VO<sub>2</sub> films were deposited on the fused silica by reactive magnetron sputtering technique. The deposition chamber was pumped to a base pressure of  $4 \times 10^{-4}$  Pa by using a turbo molecular pump, and pre-cleaned in Ar gases for 10 min to remove contamination from the target surface. The vanadium target ( $\phi$ 60 mm) of purity 99.999% was used and the power density of V target was 4.2 W cm<sup>-2</sup>. The distance of targetsubstrate was approximately 100 mm. Pure oxygen gas and argon gas were introduced to chamber at 1.8 sccm and 40 sccm, respectively. The deposition pressure and substrate temperature were maintained at 0.5 Pa and 320 °C, respectively. The deposition time was 30 min and the thickness of VO<sub>2</sub> films was controlled accurately to 150 nm. A schematic of DC magnetron sputtering is shown in Fig. 1(a). For low refractive silica (n =1.16), the SiO<sub>2</sub> sols were prepared by base catalysis of ammonia, mixed with the teraethoxysilane (TEOS), H2O, NH3 and ethanol (C<sub>2</sub>H<sub>5</sub>OH). The molar ratio of TEOS, H<sub>2</sub>O, C<sub>2</sub>H<sub>5</sub>OH and NH<sub>3</sub> was



Fig. 1 Schematic diagrams of procedure of preparation of (a) VO<sub>2</sub> films and (b) SiO<sub>2</sub> sols. (c) Schematic illustration of the structure of SiO<sub>2</sub>/VO<sub>2</sub> double-layer film.

1 : 2 : 34.2 :  $0.9^{30}$  High refractive silica (n = 1.42) was synthesized by mixing teraethoxysilane (TEOS), H<sub>2</sub>O, HCl and ethanol (C<sub>2</sub>H<sub>5</sub>OH). The molar ratio of TEOS, H<sub>2</sub>O, C<sub>2</sub>H<sub>5</sub>OH and HCl was 1 : 4 : 20 :  $0.05^{31}$  The SiO<sub>2</sub> coating with refractive index of 1.34 was prepared by mixing low refractive silica and high refractive silica with a molar ratio of 7 : 3.

The above resulting chemical reagents were stirred for 5 h and placed into an oven to age for 4 days. VO<sub>2</sub> films ( $\phi$ 30 mm, d = 3 mm) were coated with the three kinds of silicas by a dip coating process with a withdrawal speed of 7 cm  $min^{-1}$ , and then were baked at 180 °C for 24 h. The thickness of SiO<sub>2</sub> antireflection coating was about 110 nm. The schematics of preparation process of SiO<sub>2</sub> sols and dip coating process are shown Fig. 1(b). The SiO<sub>2</sub>/VO<sub>2</sub> bilayer films coated by SiO<sub>2</sub> coatings with refractive indices of 1.16, 1.34 and 1.42 are denoted as S116, S134 and S142, respectively. And the VO<sub>2</sub> film without SiO<sub>2</sub> antireflection is marked as PVO<sub>2</sub>. Fig. 1(c) illustrates the structure of  $VO_2$  film on fused quartz with a SiO<sub>2</sub> antireflection coating. The optical transmittance of the SiO<sub>2</sub>/ VO2 bilayer films were studied with a PerkinElmer Lambda 950 UV-VIS-NIR spectrophotometer from 250 to 2500 nm. A spectroscopic ellipsometer (Horiba uvisel 2) was used to characterize the refractive indices and physics thickness of SiO<sub>2</sub> coatings. The microstructure characterization of pure VO2 and SiO2/VO2 bilayer films was measured by X-ray diffraction (Rigaku Ultima IV) with a  $2\theta$  geometry. In addition, the optical transition behavior was studied by Thin film phase transition measurement system (PERFECT PTM1700) to collect the IR transmittance of films at a fixed wavelength (1550 nm) against temperature with an interval of 1.0 °C. The surface morphologies of the films were observed using a field-emission scanning electron microscope (Zeiss Supra 5S). The calculation of integral visible transmittance (T<sub>lum</sub>, 380-780 nm) and solar transmittance (T<sub>sol</sub>, 250-2500 nm) can refer to our previous work.<sup>16</sup>

### Results and discussion

The refractive index of SiO<sub>2</sub> films with wavelength were measured by using ellipsometry and fitted by Cauchy ellipsometry model. Fig. 2 shows the refractive indices of SiO<sub>2</sub> antireflection coatings dipped by base catalyzed silica, acid catalyzed silica and mixed of them on the fused quartz. The refractive index of the SiO<sub>2</sub> film prepared by base catalyzed silica was measured to be ~1.16 at 700 nm, considerably lower than that prepared by acid catalyzed silica (~1.42) or that prepared by mixed of base and acid catalyzed silica (~1.34). On the other hand, the wavelength dispersions of the refractive index and extinction coefficient of pure VO<sub>2</sub> films below and above phase transition temperature were also measured and fitted by ellipsometry, which can be found from our previous work.<sup>5</sup>

Fig. 3(a) shows the XRD patterns of both bottom-layer and double-layer thin films on quartz substrates, including the standard pattern of monoclinic (M) VO<sub>2</sub> (PDF#82-0661). All the diffraction peaks of bottom-layer and double-layer films are similar, which correspond with the characteristic pattern of the VO<sub>2</sub> M-phase. It is worth noting that no other impurity peaks (such as  $V_2O_3$ ,  $V_2O_5$  or  $V_4O_9$ ) can be observed in the XRD



Fig. 2 Dispersion curves of the refractive indices of the  $SiO_2$  AR coatings prepared on the fused quartz.

patterns, indicating the formation of high-purity single crystal VO<sub>2</sub> films. These reveal that high-quality VO<sub>2</sub> films were obtained through DC reactive magnetron sputtering at low substrate temperature and the crystalline of VO<sub>2</sub> in double-layer film was unchanged after coated with sol–gel silica antireflection coatings. Additionally, the broad peaks in the range of 10° to 25° were assigned to fused quartz substrates. The fine patterns of VO<sub>2</sub> (011) peaks is shown in Fig. 3(b). It can be obvious seen that the values of two film samples are both slightly smaller than 27.827° of VO<sub>2</sub> powder diffraction, and the value of intense diffraction peak position of the double-layer SiO<sub>2</sub>/VO<sub>2</sub> film sample is slightly smaller than 27.805° of the pure VO<sub>2</sub> film sample. The stress in films could be calculated by the formula:<sup>15</sup>

$$\sigma = \frac{E}{2\nu} \frac{d_0 - d}{d_0} \tag{1}$$

where d and  $d_0$  are the lattice distances in the strained and unstrained states, respectively. *E* and *v* are Young's modulus and Poisson's ratio of the film, respectively. The lattice coefficient could be obtained according to Bragg formula:

$$2d\sin\theta = k\lambda\tag{2}$$

where  $\theta$  is the X-ray diffraction angle, and  $\lambda$  is the X-ray wavelength. The compressive stress in double-layer SiO<sub>2</sub>/VO<sub>2</sub> film sample is larger than that of pure VO<sub>2</sub> film after calculation from the above formulas.

Fig. 4 shows the top-view SEM images of pure VO<sub>2</sub> and SiO<sub>2</sub>/VO<sub>2</sub> bilayer films. For the pure VO<sub>2</sub> film, rice-like nanoparticles scattered on the surface, indicating the good crystallinity of the sample. The morphology is porous for the sample S116, while the sample S142 behaved a denser structure without any pores on the surface. The surface morphology of sample S134 shows both characteristic mentioned above. Moreover, the cross-sectional SEM image of sample S116 is shown in the inset image of Fig. 4, in which an obvious interface between the 110 nm SiO<sub>2</sub> antireflective layer and 150 nm VO<sub>2</sub> film can be observed.



Fig. 3 XRD spectra of the pure VO<sub>2</sub> film and SiO<sub>2</sub>/VO<sub>2</sub> film: (a) normalized patterns; (b) fine patterns of VO<sub>2</sub> (011) peaks.

Fig. 5(a) shows the temperature-dependent transmittance of the pure VO<sub>2</sub> film and S116 bilayer film sample at  $\lambda = 1550$  nm. Thermal hysteresis loop is evident for both film samples and the semiconductor-to-metal transition occurred, indicating that the double-layer SiO<sub>2</sub>/VO<sub>2</sub> film sample maintained the phase transition properties. Compared with the pure VO<sub>2</sub> film, the enhancement of transmittance at  $\lambda = 1550$  nm is obvious, and the highest value can reach 72% for the sample S116. The tunable-RI SiO<sub>2</sub> coatings can significantly suppress the optical reflection losses and improve light transmission. Fig. 5(b) shows the Standard Gauss fitting derivative logarithmic plots, which were obtained by taking the derivative of the logarithmic transmittance with respect to the temperature of film sample. Phase transition temperature can be defined as  $T_c = (T_l + T_h)/2$ , and the thermal hysteresis width was calculated by  $\Delta H = T_h - T_l$ . The values of phase transition temperatures for pure VO<sub>2</sub> and S116 film sample are 63.5 °C and 60 °C, respectively, which are lower than 68 °C of the bulk VO<sub>2</sub>. Moreover, the phase transition temperature of sample S116 is lower than that of pure VO<sub>2</sub> film. The main reason is that the larger compressive



Fig. 4 Top-view SEM images of pure VO<sub>2</sub> and SiO<sub>2</sub>/VO<sub>2</sub> bilayer films.



Fig. 5 (a) Transmittance hysteresis loops of pure VO<sub>2</sub> film and SiO<sub>2</sub>/VO<sub>2</sub> bilayer films at  $\lambda = 1550$  nm and (b) corresponding dT/dt vs. temperature curve for film samples PVO<sub>2</sub> and S116.

stress existed in the double-layer film sample compared with the pure VO<sub>2</sub> film sample, which has been discussed in the XRD analysis. Our previous work<sup>32</sup> reported that the compressive stress changed the phase transition temperature of VO<sub>2</sub> film samples by applying TiO<sub>2</sub> buffer layers. The width of the hysteresis loop of sample S116 is 14.5 °C, which is also smaller than that of pure VO<sub>2</sub> film sample (18.5 °C). These results are different from other reports, which usually revealed that adding SiO<sub>2</sub> antireflection coatings would increase the  $T_c$  and  $\Delta H$  to a certain extent due to the existence of SiO<sub>2</sub> as thermal insulation.<sup>24,28</sup> The main reason of our experimental results may be the special porous morphology for the sample S116 with low refractive index.

To investigate the effect of RI-fixed SiO<sub>2</sub> coatings on the optical properties of the VO<sub>2</sub> films, the transmittance spectra were examined as shown in Fig. 6(a). The visible transmittance (at  $\lambda = 700$  nm) and IR transmittance modulation (at  $\lambda = 2500$  nm) of the film samples were calculated, as shown in Fig. 6(b). The transmittance at  $\lambda = 700$  nm for the samples with SiO<sub>2</sub> antireflection coatings is higher than that of the single-layer VO<sub>2</sub> film, in which the sample with SiO<sub>2</sub> refractive index of

1.42 behaved the best. The visible transmittance at  $\lambda = 700$  nm increased from 47% to 66% as the refractive index of SiO<sub>2</sub> antireflection coating increased from 1.16 to 1.42.

To fully display the superior optical properties of single-layer  $VO_2$  and  $SiO_2/VO_2$  double-layer films, the luminous transmittance ( $T_{lum}$ ) and solar spectral transmittance ( $T_{sol}$ ) of film samples were calculated based on the measured transmittance using the following eqn (3) and (4):

$$T_{\rm sol} = \int \varphi_{\rm sol}(\lambda) T(\lambda) d\lambda / \int \varphi_{\rm sol}(\lambda) d\lambda$$
(3)

$$T_{\rm lum} = \int \varphi_{\rm lum}(\lambda) T(\lambda) d\lambda \bigg/ \int \varphi_{\rm lum}(\lambda) d\lambda$$
 (4)

here,  $T(\lambda)$  represents the transmittance,  $\varphi_{sol}$  is the solar spectral irradiance for mass of 1.5. The angle between the sun and the horizon is above 37° and the wavelength is 280–2500 nm.  $\varphi_{lum}$  is the standard luminous efficiency function of photonic vision and the wavelength for the  $\varphi_{lum}$  is 380–780 nm. The values of  $\Delta T_{sol}$  and  $T_{lum(avg)}$  can be obtained as follows:



Fig. 6 (a)Transmittance spectra of pure VO<sub>2</sub> film and bilayer films. Solid lines represent the transmittance recorded at 25 °C and dotted lines measured at 80 °C. (b)  $T_{\text{vis}}$  at  $\lambda = 700$  nm and  $\Delta T_{\text{IR}}$  at  $\lambda = 2500$  nm for the samples.

Table 1 Solar switching efficiency ( $\Delta T_{sol}$ ) and luminous transmittance ( $T_{lum}$ ) of the pure VO<sub>2</sub> film and SiO<sub>2</sub>/VO<sub>2</sub> bilayer films compared with the reported studies

Samples	$T_{ m sol,l} \left[\% ight]$	$T_{\rm sol,h} \left[\%\right]$	$\Delta T_{ m sol} \left[\% ight]$	$T_{\rm lum,l}$ [%]	$T_{\text{lum,h}}$ [%]	$T_{\rm lum(avg)}$ [%]	$\Delta T_{ m lum}$ [%]
$PVO_2$ (this work)	44.57	38.32	6.25	37.06	40.10	38.58	3.04
S116 (this work)	50.71	42.43	8.28	40.81	43.04	41.93	2.23
S134 (this work)	54.14	45.99	8.15	47.77	48.37	48.07	0.60
S142 (this work)	57.83	49.32	8.51	50.11	50.76	50.44	0.65
$VO_2$ (a) SiO <sub>2</sub> arrays <sup>26</sup>	_	_	6.70	_	_	43.50	_
$SiO_2/VO_2$ (ref. 27)	_	_	7.62	_	_	47.70	_
$\alpha$ -SiO <sub>2</sub> /VO <sub>2</sub> / $\alpha$ -SiO <sub>2</sub> (ref. 33)	36.50	32.00	4.50	35.20	34.80	35.00	0.40
$TiO_2/VO_2$ (ref. 34)	46.25	39.26	6.99	49.15	45.05	47.10	4.10
$TiO_2(R)/VO_2(M)/TiO_2(A)^{35}$	33.80	23.60	10.20	30.10	27.80	28.95	2.30
Moth-eye structure <sup>20</sup>	52.10	45.00	7.10	43.60	45.30	44.50	-1.70
$VO_2/SiO_2/TiO_2$ coating <sup>36</sup>	28.83	13.55	15.29	17.81	18.23	18.02	-0.42

$$\Delta T_{\rm sol} = T_{\rm sol,l} - T_{\rm sol,h} \tag{5}$$

$$T_{\rm lum(avg)} = (T_{\rm lum,l} + T_{\rm lum,h})/2$$
 (6)

here,  $T_{\rm sol,l}$  indicates the solar transmittance in semiconductor state and  $T_{\rm sol,h}$  indicates the solar transmittance in metal state.  $T_{\rm lum,l}$  and  $T_{\rm lum,h}$  mean the luminous transmittance in the low temperature state and high temperature state, respectively.

The solar switching efficiency  $(\Delta T_{sol})$  and visible transmittance  $(T_{lum})$  of the pure VO<sub>2</sub> film and bilayer films are shown on Table 1. It is obvious that  $T_{\rm lum}$  and  $\Delta T_{\rm sol}$  of the SiO<sub>2</sub>/VO<sub>2</sub> films were all higher than the pure VO<sub>2</sub> film. Furthermore, the  $T_{\text{lum,l}}$  and  $T_{\text{lum,h}}$  of these samples both increased obviously as the refractive indices of SiO<sub>2</sub> coatings increased from 1.16 to 1.42, and the values of  $\Delta T_{sol}$  also exhibited a slightly increasing trend at the same time. The maximum values of  $T_{\rm lum}$  and  $\Delta T_{\rm sol}$ for film sample S142 can reach 50.44% and 8.51%, respectively. This result was better than the values of reported  $VO_2$   $O_2$ arrays prepared by rapid thermal annealing of sputtered vanadium films,26 SiO2/VO2 double-layered films obtained vis plasma enhanced chemical vapor deposition,<sup>27</sup> a-SiO<sub>2</sub>/VO<sub>2</sub>/a-SiO<sub>2</sub> multi-layered films and TiO<sub>2</sub>/VO<sub>2</sub> films deposited by radio frequency reactive magnetron sputtering.33,34 Although the TiO<sub>2</sub>(R)/VO<sub>2</sub>(M)/TiO<sub>2</sub>(A)<sup>35</sup> multi-layered films made through radio frequency reactive magnetron sputtering and VO<sub>2</sub>/SiO<sub>2</sub>/ TiO<sub>2</sub> (ref. 36) films fabricated vis atmospheric-pressure chemical vapor deposition behaved higher  $\Delta T_{sol}$  than our result, the values of their  $T_{lum(avg)}$  were lower. More detailed results about recent studies were summarized in Table 1. In this work, the formation of smoother and denser film surface after SiO<sub>2</sub> coating can decrease the light scattering of the sample and enhance the visible transmittance. These results indicate that applying SiO<sub>2</sub> antireflection coatings with tunable refraction index can be an efficient way to enhance the visible transmittance of VO<sub>2</sub> films simultaneously and continuously.

#### 4. Conclusion

In this work,  $SiO_2/VO_2$  bilayer films were synthesized successfully by magnetron sputtering and sol-gel method. The crystallization properties of  $VO_2$  films is essentially unchanged by applying  $SiO_2$  top layer. The bilayer films can behave high transmittance and good thermochromic performance when compared with the single-layer pure VO<sub>2</sub> film. For the sample S142, the maximum value of  $T_{\rm lum}$  can reach 50.44%. For the sample S116, the width of hysteresis loop and transition temperature are 14.5 °C and 60 °C, respectively, which are smaller than those of pure VO<sub>2</sub> film sample (18.5 °C and 63.5 °C). Moreover, the  $T_{\rm lum}$  of these bilayer films increased obviously as the refractive index of SiO<sub>2</sub> antireflective layer increased from 1.16 to 1.42, and the  $\Delta T_{\rm sol}$  exhibited a slightly increasing trend. Hence, the enhancement of  $T_{\rm lum}$  and  $\Delta T_{\rm sol}$  simultaneously and continuously provides a meaningful solution for VO<sub>2</sub>-based thermochromic energy-efficient smart windows.

### Conflicts of interest

There are no conflicts to declare.

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