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Optical properties of Ti_3SiC_2 and Ti_4AlN_3

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The dielectric functions of the *MAX* phases, Ti_3SiC_2 and Ti_4AlN_3 , have been determined from first principles calculations. We compared the dielectric functions and the reflectivity spectra of Ti_3SiC_2 and Ti_4AlN_3 with those of TiC and TiN. The optical spectra were analyzed by means of the electronic structure, which provides theoretical understanding of the conduction mechanism of these two phases. We found that Ti_4AlN_3 can be used to avoid solar heating and also increase the radiative cooling due to the increased thermal emittance as compared to TiN. Ti_4AlN_3 can therefore be a candidate coating material for temperature control of space vehicles. © 2008 American Institute of Physics. [DOI: 10.1063/1.2938862]

$M_{n+1}AX_n$ ($n=1-3$), which is the generic chemical formula for the so called *MAX* phases in literature, represents a class of technologically important solids exhibiting unusual properties associated with both metals and ceramics.¹ Here, M is an early transition metal, A is a group IIIA or IVA element, and X is either C and/or N. There are nearly 50 *MAX* phases reported by experimentalists so far. However, only three M_3AX_2 (Ti_3SiC_2 , Ti_3GeC_2 , and Ti_3AlC_2) phases and two bulk M_4AX_3 , i.e., Ti_4AlN_3 ² and Ta_4AlC_3 ³ are known. Generally speaking, the *MAX* phases are good thermal and electrical conductors. They exhibit high strength at high temperatures, but are relatively soft and can be machined using conventional high-speed tools without lubrication. They demonstrate good thermal shock and oxidation resistance. The most intensively studied *MAX* phase is Ti_3SiC_2 . Experimental investigations showed that Ti_3SiC_2 has Young's modulus higher than 330 GPa,¹ but exhibits fully reversible plasticity. It also exhibits high electrical and thermal conductivities, but negligible thermoelectric power. The negligible thermoelectric power is attributed to the fact that both electrons and holes contribute to the conductivity of Ti_3SiC_2 .⁴ On the other hand, Ti_4AlN_3 has a lower electrical conductivity than other *MAX* phases.⁵ Even though numerous calculations have been carried out on the electronic structures of *MAX* phases, especially on Ti_3SiC_2 ,⁶⁻¹² the optical properties of the *MAX* phases have not received adequate attention from neither experimentalists nor theorists. Herein, we present results obtained through our theoretical studies of the optical properties of both Ti_3SiC_2 and Ti_4AlN_3 , attempting to contribute to the understanding of the conduction mechanisms of these two ternaries.

The calculations have been done using the full potential linear muffin-tin orbital¹³ method. The exchange and correlation part of the potential was calculated using the local density approximation with the Hedin-Lundqvist¹⁴ parametrization. The integration over the Brillouin zone was done using the special point sampling¹⁵ with 193 k points in the

irreducible Brillouin zone and the details were given elsewhere.¹⁶ The dielectric function, $\epsilon(\omega)=\epsilon_1(\omega)+i\epsilon_2(\omega)$, fully describes the optical properties of a medium at all photon energies, $\hbar\omega$. The ($q=0$) dielectric function was calculated in the momentum representation, which requires matrix elements between occupied and unoccupied eigenstates. To be specific, the imaginary part of the dielectric function can be calculated from

$$\epsilon_2^{ij}(\omega) = \frac{4\pi^2 e^2}{\Omega m^2 \omega^2} \sum_{knn'\sigma} \langle \mathbf{k}n\sigma | p_i | \mathbf{k}n'\sigma \rangle \langle \mathbf{k}n'\sigma | p_j | \mathbf{k}n\sigma \rangle f_{kn}(1 - f_{kn'}) \delta(e_{kn'} - e_{kn} - \hbar\omega).$$

In the equation above, e is the electron charge, m is its mass, Ω is the crystal volume, and f_{kn} is the Fermi distribution. Moreover, $|\mathbf{k}n\sigma\rangle$ (is the crystal wave function corresponding to the n th eigenvalue with crystal momentum \mathbf{k} and spin σ). With our spherical wave basis functions, the matrix elements of the momentum operator were calculated in spherical coordinates. The evaluation of the matrix elements was done over the muffin-tin region and the interstitial separately. The integration over the primitive cell was done in a way similar to what Oppeneer *et al.*¹⁷ and Gasche¹⁸ did in their calculations. The correct symmetry for the dielectric constant was obtained by averaging the calculated dielectric function. The real part of the dielectric function was derived through the Kramers-Kronig relations.

It should be noted that metal or metal-like conductors include an intraband contribution from the conduction electrons that is *not* treated in the aforementioned calculations that only include interband excitations. We therefore chose to add a conventional Drude contribution to the calculated results. The Drude expression for the imaginary part of the dielectric function is conventionally written as

$$\epsilon_2^\omega = \frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)}.$$

Here, ω_p is the plasma frequency and τ is the relaxation time. In principle, this contribution is valid for all frequencies, and

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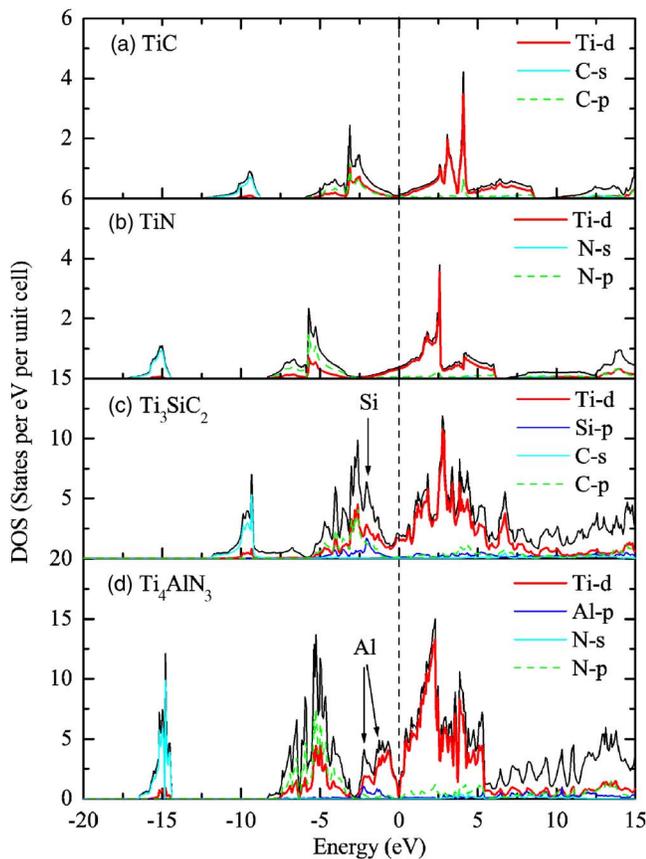


FIG. 1. (Color online) The DOS for TiC, TiN, Ti_3SiC_2 , and Ti_4AlN_3 . In all cases, the Fermi energy was shifted to zero.

we note that it will be significant for low frequencies, i.e., <1 eV. For high frequencies, the Drude contribution to ϵ_2 vanish. The expression contains two parameters, ω_p and τ . With some reservations for contributions to the “broadening” and “screening” by higher lying excitations, ω_p is the frequency where the real part of the dielectric function goes through zero from below and the imaginary part approaches zero from above. The relaxation time is a characteristic time between electron-phonon collisions. The inverse, i.e., $1/\tau$, the collision frequency, often given by the symbol Γ , is a measure of the broadening of the phenomenological Drude feature. Although it is not formally well founded, there is a correlation between the relaxation times obtained in the Drude expression (describing transverse response) and the relaxation time that characterizes the (longitudinal) electrical conductivity. We shall use the two parameters ω_p and \hbar/τ for fitting the calculated dielectric function to the experimental one over the entire energy interval.

Another important parameter that governs the optical properties of a metal or metal-like conductor is the onset of the interband transitions. It is known that in TiC—where the interband transition occurs at energies <0.1 eV—there is almost no free-electron-like region. In contrast, TiN exhibits a free-electron-like region, below 2.5 eV, with a high and constant reflectance.¹⁹ Early band structure calculations by Neckel *et al.*²⁰ explained the different onset of transition energy for TiC and TiN. The position where E_F is located is the key to the onset of the interband transition energy or plasma energy. In TiC [Fig. 1(a)], E_F is located at the minimum of the density of states (DOS) valley, it is a semimetal, and low in conductivity. While in TiN [Fig. 1(b)], E_F is situated

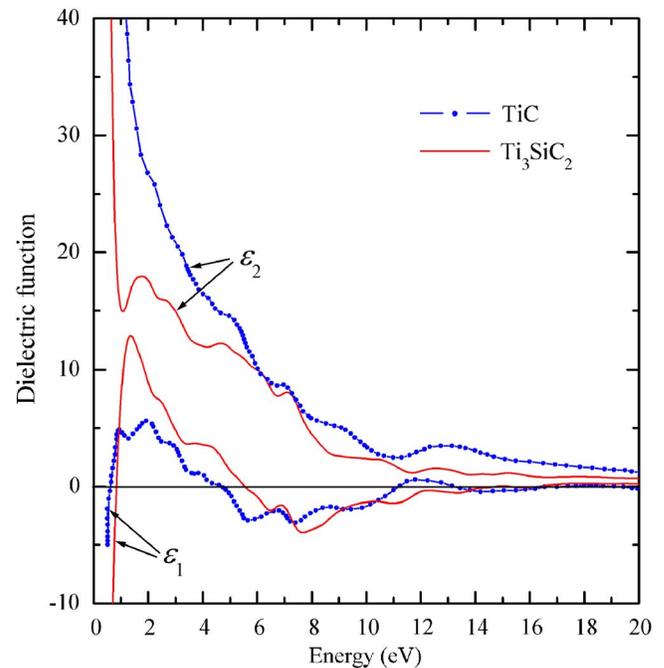


FIG. 2. (Color online) The calculated dielectric functions of Ti_3SiC_2 in comparison to experimental dielectric functions of $\text{TiC}_{0.9}$ (Ref. 23). The calculated spectra have been fitted by the addition of a Drude term.

among the metal Ti-*d* dominated states and the free-electron-like behavior comes from the *d* electrons. We know that electrical conductivity is directly related to the plasma frequency,²¹ and in the simplest approximation, it is proportional to the DOS at E_F . The addition of Si to TiC moves E_F out from the energy minimum [Fig. 1(c)]. We can observe the obvious contribution from the Ti-*d* band to the DOS at E_F . The plasma energy of Ti_3SiC_2 increases in comparison to TiC. In contradistinction, the Al addition to TiN moves E_F down to the bottom of the DOS valley [Fig. 1(d)], and therefore the plasma energy decreases. This also suggests that Ti_3SiC_2 should have a higher plasma frequency than Ti_4AlN_3 , which is contrary to the case of TiC compared with TiN.¹⁹

In Fig. 2(a) a Drude term with plasma frequency $\omega_p = 2$ eV (Ref. 22) and relaxation energy $\hbar/\tau = 0.3$ eV was added to the dielectric function of Ti_3SiC_2 . Its effect is to increase the low-energy part of the spectrum. The dielectric function of Ti_3SiC_2 was compared with that of $\text{TiC}_{0.9}$.²³ In $\epsilon_1(\omega)$, we can see that the double peak structure centered at 1.7 eV for TiC is replaced with a sharp peak at around 2 eV for Ti_3SiC_2 . In $\epsilon_2(\omega)$, the spectra differ at low energy, which is the result of the dramatic electronic structure change near the Fermi level, induced by the addition of Si layer along the TiC (111) direction.¹⁰

The dielectric functions of Ti_4AlN_3 and TiN (Ref. 24) are compared in Fig. 3. A Drude term with plasma frequency $\omega_p = 1$ eV (Ref. 22) and relaxation energy $\hbar/\tau = 0.3$ eV was included for Ti_4AlN_3 . All the calculated spectra were broadened with a Gaussian function with a width of 0.05 eV.

The reflectivity as a function of energy is presented in Fig. 4. We can see a sharp reflectance drop at ω_p for TiN, between 2 and 3 eV, which is characteristic of high conductance. TiN has high reflectivity in the infrared, and low reflectivity (transparency) for shorter wavelengths.²⁵ This similarity to the optical properties of gold makes TiN thin films

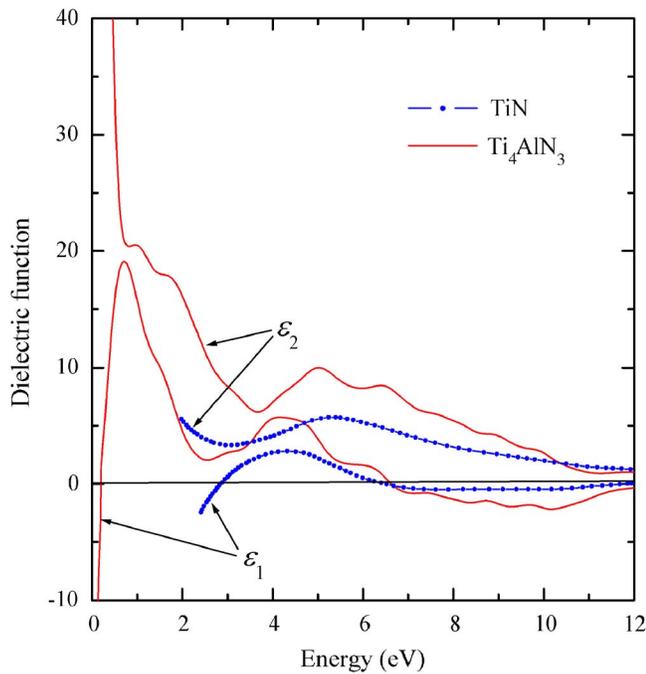


FIG. 3. (Color online) The calculated dielectric functions of Ti_4AlN_3 in comparison to experimental dielectric functions of TiN (Ref. 24). The calculated spectra have been fitted by the addition of a Drude term.

promising as low-emitting window coatings.¹⁹ The low reflectance in the region of blue and violet light (2.8–3.5 eV) for TiN gives its goldlike color.²⁶ With Al addition to TiN, the reflectivity decreases dramatically in the infrared region and increases in the region of visible light (Fig. 4). The decrease of the infrared reflectivity is due to the lower plasma frequency. The reflectivity minimum of 0.3 for Ti_4AlN_3 is higher than the 0.2 for pure TiN. Also, the dip shifts from 2.8 to 3.7 eV, i.e., outside the visible light region.

We note the difference between the reflectance spectra of Ti_4AlN_3 and TiN. The strong edge and color of the latter is absent in the MAX compounds. The spectrum of Ti_4AlN_3 is thus nonselective, similar to those of transition metals. This implies that solar heating is reduced and the infrared emittance, $E=1-R$, is significantly enhanced as compared to that of the noble metals, aluminum or even iron. The equilibrium

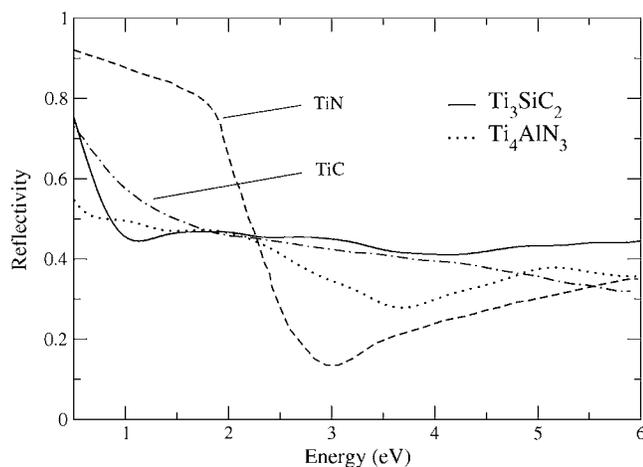


FIG. 4. Reflectivity spectra of Ti_3SiC_2 and Ti_4AlN_3 together with those of TiC (Ref. 19) and TiN (Ref. 19).

temperature of a Ti_4AlN_3 surface will therefore be moderate in strong sunlight. This combined with the good mechanical strengths as well as the thermal and chemical inertness has led to an interest in Ti-Al-N alloys, as potential materials for temperature control of space vehicles. The reflectance of Ti_3SiC_2 is similar to that of TiC: with almost a constant value in the region we explored. The constant reflectance in the visible region makes Ti_3SiC_2 appear metallic gray.

We studied the optical properties of Ti_4AlN_3 and Ti_3SiC_2 . The conduction mechanisms of these two phases have been analyzed by means of their electronic structures. Based on our results, Ti_4AlN_3 has the potential to be used as a coating on spacecrafts to avoid solar heating and also increase the radiative cooling as a result of its increased thermal emittance as compared to TiN. The MAX phases are therefore candidate materials for coatings in future space missions to Mercury.

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