Optical filtering properties of TiO$_2$/Al$_2$O$_3$ heterostructures from first principles

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This study combines the use of the full potential linear-augmented plane wave method (FP-LAPW) within the framework of the density functional theory (DFT) and the optical matrix approach for modeling the multilayer assembly. A new class of heterostructures with sufficient number of alternating layers of rutile-TiO$_2$ (as a high index material) and $\alpha$-Al$_2$O$_3$ (as a low index material) are proposed and their transmittance spectra are investigated. This study shows that the number of alternating layers, and the thickness and arrangement of them should be considered in making a heterostructured filter. The relation between heterostructure parameters and narrow-band-pass peaks of transmittance spectra is investigated. The proposed model seems to be successful in predicting the optical behavior of heterostructures and simulations agree well with the experimental observations. In addition, our model is very flexible and the effect of other parameters such as incident angle and light polarization can be easily investigated.

Keywords: Optical properties; DFT; Abeles matrix theory; FP-LAPW; TiO$_2$/Al$_2$O$_3$ heterostructure; band pass filter.

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1. Introduction

Dielectric thin-film-based multilayer coatings are widely used in optics and electronics. For example there are a variety of optical coatings needed on laser bar facets to make them functional.$^{1-4}$ A narrow-band filter can be used as a frequency-selective filter which is an important device in signal processing. It can also work as a demultiplexer for the wavelength division multiplexing (WDM) systems. The design of optical coatings such as filters and antireflective coatings based on multilayer systems requires detailed knowledge of the optical properties of the materials.

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The dispersion curves and the growth rates of the dielectric films must be accurately determined. Several factors such as the deposition technique and conditions (e.g., temperature and pressure) will affect thin film properties. Many manufacturers chose to use a combination of silicon and aluminium oxide for the mirror stacks and typically 6–8 layers will be sufficient in this case. The problem with using this combination below one micron is that the silicon becomes absorbing and limits the ultimate reflectance. Using nonabsorbing materials such as TiO₂/SiO₂ or TiO₂/Al₂O₃ can result in a reflectance as high as 99% or greater, depending on deposition conditions. Bulk TiO₂/Al₂O₃ ceramics have historically been used as structural refractory materials because of their low thermal expansion, thermal shock resistance, and high temperature stability. Recent interest in TiO₂/Al₂O₃ ceramics extends to thin films and nanocomposites that depend upon the materials' response to light, including tailored refractive index films, transparent dielectrics and photocatalytic applications. Experimental reports about optical properties of TiO₂/Al₂O₃ multilayers can be seen in other studies.

In this work, we study the role of thicknesses (especially the thickness of 8th layer) and the arrangement of layers in the transmittance spectra of TiO₂/Al₂O₃ heterostructures, within the framework of density functional theory (DFT) and Abeles matrixes theory. Since the refractive index of semiconductor which is a measure of its transparency to incident radiation, and the energy gap which determines the threshold for absorption of photons in semiconductors, are two fundamental physical aspects that characterize the optical properties of crystals, first we calculate the dielectric function of materials using the DFT. Then the Abeles matrix theory is used to simulate the optical transmission, absorption and reflection of heterostructures. Our model is very flexible and the role of many parameters like thicknesses, arrangement of layers, incident angle and light polarization can be easily investigated.

The rest of this paper is organized as follow: In the next section the calculation method is discussed. A brief discussion about the transmittance spectra of heterostructures is given in Sec. 3. Section 4 presents a brief summary and conclusion of this study.

2. Calculation Method
In order to study the role of different parameters such as the thickness and arrangement of layers, several samples of 15-fold heterostructures have been designed and their transmittance spectra have been investigated. In the first step of our study, we have performed first principle calculations based on the state-of-the-art all electron FP-LAPW method to solve the Kohn–Sham equations within the framework of WIEN2K package. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhoft was used for the exchange-correlation potential. Basis functions are expanded in combinations of spherical harmonic functions inside nonoverlapping spheres at the atomic sites (muffin-tin spheres) and in plane waves in the

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interstitial regions. Inside the muffin-tin spheres of radius $R_{MT}$, the $l$-expansion of
the wave function were carried out up to $l_{\text{max}} = 10$. The convergence parameter
$RK_{\text{max}}$, which controls the size of the basis sets in these calculation, was set to 7.
The $G_{\text{max}}$ parameter was taken to be 12.0 Bohr$^{-1}$. The number of $k$ points in
the irreducible Brillouin zone for rutile-$\text{TiO}_2$ and $\alpha$-$\text{Al}_2\text{O}_3$ were chosen to be 280 and
288, respectively. The muffin-tin radii for Al, Ti, $\text{O}_{\text{TiO}_2}$ and $\text{O}_{\text{Al}_2\text{O}_3}$ were taken to
be 1.57, 1.93, 1.75 and 1.91 a.u., respectively. In the second step we have calculated
the optical transmittance of heterostructures within the framework of optical ma-
trices model.$^{21-23}$ In the following we present a brief summary of our calculations
and mathematical relations.

The optical properties of matter is described by the transverse dielectric function
$\varepsilon(\omega)$. The imaginary part of dielectric function is represented by $\varepsilon_2(\omega)$ and the real
part of dielectric function is represented by $\varepsilon_1(\omega)$. The imaginary part of dielectric
function is calculated as follows:

$$
\varepsilon_2(\omega) = \frac{V_e^2}{2\pi\hbar^2\omega^2} \int d^3k \sum_{n,n'} |\langle kn|p|kn'\rangle|^2 f(kn)
\times (1 - f(kn')) \delta(E_{kn} - E_{kn'} - \hbar\omega),
$$

(1)

where the sum is over all possible transitions from occupied to the unoccupied
states. $\hbar\omega$ is the energy of the incident photon, $p$ is the momentum operator
$-i\hbar(\partial/\partial x)$, $|kn\rangle$ is the eigenfunction with eigenvalue $E_{kn}$ and $f(kn)$ is the Fermi
distribution function. The evaluation of the matrix elements of the momentum
operator in Eq. (1) is done over the muffin-tin and the interstitial regions sepa-
rateely.$^{21,22}$ Generally, the elements of imaginary dielectric tensor are not equal and
the average value was used in this study:

$$
\varepsilon_2(\omega) = \frac{\varepsilon_{2xx}(\omega) + \varepsilon_{2yy}(\omega) + \varepsilon_{2zz}(\omega)}{3}.
$$

(2)

When the imaginary tensor calculated using DFT theory, the real part of dielectric
function can be determined from the imaginary part using the Kramers–Kronig
relation.$^{23,24}$ We also have used the mean value for $\varepsilon_1(\omega)$.

The refractive index ($n$) and extinction coefficient ($k$) of materials are calculated
using the following relations:

$$
n = \left(\frac{[\varepsilon_1^2 + \varepsilon_2^2]^{1/2} + \varepsilon_1}{2}\right)^{1/2},
$$

(3)

$$
k = \left(\frac{[\varepsilon_1^2 + \varepsilon_2^2]^{1/2} - \varepsilon_1}{2}\right)^{1/2}.
$$

(4)

The complex refractive index of $j$th layer is given by:

$$
\tilde{n}_j = n_j + ik_j.
$$

(5)
The incidence angle of light in $j$th layer ($\theta_j$) can be determined by the Snell’s law:

$$\tilde{n}_j \sin \theta_j = \tilde{n}_0 \sin \theta_0.$$  \hspace{1cm} (6)

In the above relation, $\tilde{n}_0$ and $\theta_0$ are the refractive index and incidence angle in vacuum, respectively. Phase shift due to $j$th layer ($\delta_j$) is then given by:

$$\delta_j = \frac{2\pi \tilde{n}_j d_j \cos \theta_j}{\lambda}.$$  \hspace{1cm} (7)

In the relation (7), $d_j$ is the thickness of $j$th layer and $\lambda$ is the light beam wavelength.

The impedance of $j$th layer for $s$-polarization and $p$-polarization is defined by:

$$\eta_j = \sqrt{\varepsilon_0 \mu_0 \tilde{n}_j \cos \theta_j} \quad \text{(for s-polarization)},$$

$$\eta_j = \sqrt{\varepsilon_0 \mu_0 \tilde{n}_j \cos \theta_j} \quad \text{(for p-polarization)}.$$  \hspace{1cm} (8)

In the relation (8), $\varepsilon_0$ is the permittivity of free space and $\mu_0$ is the permeability of free space.

In the multilayer system, the idea of matching the electric $E$ and magnetic $H$ fields of incident light at the interfaces of layers yield the matrix relation:

$$\begin{bmatrix} B \\ C \end{bmatrix} = \left\{ \prod_{j=1}^{N} \begin{bmatrix} \cos \delta_j & i \sin \delta_j/\eta_j \\ i \eta_j \sin \delta_j & \cos \eta_j \end{bmatrix} \right\} \begin{bmatrix} 1 \\ \eta_{\text{sub}} \end{bmatrix}.$$  \hspace{1cm} (9)

The $2 \times 2$ matrix on the right-hand side of this equation is known as the characteristic matrix of $j$th thin film and the $2 \times 1$ matrix on the left-hand side of this equation is known as the characteristic matrix of assembly. $B$ and $C$ are total electric and magnetic field amplitudes of the propagating light in the medium. $\eta_{\text{sub}}$ is the impedance of the substrate and $\eta_0$ is the impedance of vacuum.

Optical transmittance ($T$), absorbance ($A$) and reflectance ($R$) can be derived by the following relations:

$$T = \frac{4\eta_0 \text{real}(\eta_{\text{sub}})}{(\eta_0 B + C)(\eta_0 B + C)^*},$$

$$A = \frac{4\eta_0 \text{real}(BC^* - \eta_{\text{sub}})}{(\eta_0 B + C)(\eta_0 B + C)^*},$$

$$R = \left( \frac{\eta_0 B - C}{\eta_0 B + C} \right) \left( \frac{\eta_0 B - C}{\eta_0 B + C} \right)^* = 1 - T - A.$$  \hspace{1cm} (10-12)

3. Result and Discussion

Calculated imaginary and real parts of dielectric function of our materials are shown in Figs. 1(a) and 1(b), respectively. It can be seen that the imaginary curve of TiO$_2$ (Al$_2$O$_3$) has negligible values at energies under 3.3 eV (8.8 eV). So, it is
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expected that both of them represent negligible absorption within the visible and infrared wavelength ranges but the absorption at shorter wavelengths (for example at ultraviolet region) is not negligible. Figure 1(b) shows that the real part of dielectric function for Al$_2$O$_3$ has small variation at energies under 15 eV, but the curve of TiO$_2$ has large variations and achieve negative values at energies above 9 eV.

The values of refractive index ($n$) and extinction coefficient ($k$) of TiO$_2$ and Al$_2$O$_3$ are represented in Figs. 1(c) and 1(d), respectively. Figure 1(c) shows that the refractive index curves of TiO$_2$ and Al$_2$O$_3$ have similar patterns at wavelengths above 400 nm but the refractive index curve of TiO$_2$ has larger values. Figure 1(d) shows that the extinction coefficient of TiO$_2$ (Al$_2$O$_3$) is negligible at wavelengths above 150 nm (400 nm).

The role of number of layers in transmittance spectra is represented in Fig. 2. (2x is the number of layers). This figure shows that when the number of alternating layers increases the heterostructure is able to represent filtering property. It should be noted that when the refractive index ratio is small, more layers will be needed. Another important result of this figure is that when the number of layers increases, the narrow-band pass peak tends towards higher wavelengths. Fig. 3 shows the transmittance spectra for (TiO$_2$–Al$_2$O$_3$)$_{10}$. As can be seen in this figure, when the thicknesses of TiO$_2$ layers are small, the number of layers cannot play its role
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![Graph 1](image1.png)

**Fig. 2.** Variation of transmittance spectra for (TiO$_2$–Al$_2$O$_3$)$_x$ when $x$ increases.

![Graph 2](image2.png)

**Fig. 3.** Transmittance spectra of (TiO$_2$–Al$_2$O$_3$)$_{10}$ for small thickness of TiO$_2$ layers.

in creating filtering property. So, making a heterostructured filter needs to consider both thicknesses and number of layers. According to HLHLHLH(L)HLHLHLH arrangement, we have proposed six samples in which each sample has three branches (a)–(c). Each heterostructure has 15 layers (Table 1). Contrary to the second three samples, in the first three samples (regardless to the 8th layer) the thickness of TiO$_2$ layers are larger than Al$_2$O$_3$ layers. Table 1 shows that the inverse of sample 1 is sample 4, the inverse of sample 2 is sample 5 and the inverse of sample 3 is sample 6. Similar samples have been proposed by Szeghalmi et al. to measure the transmittance spectra, experimentally.\textsuperscript{15}
Table 1. Thickness of layers in our samples.

<table>
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<tr>
<th>Layers</th>
<th>Sample 1</th>
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<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
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<td>b</td>
<td>c</td>
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</table>
Fig. 4. Transmittance spectra for different samples of this study.

In the following section, we have shown the transmittance spectra for all of our samples in Fig. 4. This figure shows that all samples have narrow-band-pass peaks (NBPP) in their transmittance spectra. For example sample 1 has NBPP in the visible region, while sample 6 has NBPP in the infrared region. Several important results can be deduced from Fig. 4. It can be seen that when the thickness of layer increases, the NBPP tends to higher wavelengths (for example sample 6 has higher values of $\lambda_{NBPP}$ compared to others). Another important result is that when the thickness of TiO$_2$ layers are larger than Al$_2$O$_3$ layers, the NBPP shifts to higher wavelengths (for example sample 4 has higher values of $\lambda_{NBPP}$ compared to sample 1). The other important result is that when the thickness of 8th layer increases, the NBPP shifts toward higher wavelengths (for example sample 1c has higher values of $\lambda_{NBPP}$ compared to sample 1a). Szeghalmi et al. have reported similar results using atomic layer deposition (ALD) technique.\textsuperscript{15}

In the following, the relation between $\lambda_{NBPP}$ and the thickness of 8th layer is represented in Fig. 5. This figure expressed the previous results more clearly. As can be seen, the relation between $\lambda_{NBPP}$ and the thickness of 8th layer is linear but the second three samples have larger incline compared to first three samples. As we mentioned before, this figure shows that the $\lambda_{NBPP}$ increases with both thickness of layers (for example sample 3 compared to sample 1) and thickness of TiO$_2$ layers (for example sample 4 compared to sample 1). An experimental study which carried out by Szeghalmi et al.\textsuperscript{15} shows that the relation between $\lambda_{NBPP}$ and the thickness of 8th layer is linear.

Finally, we can combine our samples in order to filter more wavelengths. We can generate desired NBPPs at different positions of spectra using mixture of our samples. For example the heterostructure 1b–4b in Fig. 6 has a main NBPP in the
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Fig. 5. Variation of NBPP wavelength when the thickness of 8th layer changes.

Fig. 6. Transmittance spectra for some combinations of our samples.

ultraviolet region while the heterostructure 2c–3b–6b can represent main NBPP in the visible region.

To sum up, a satisfactory coincidence of both the theoretical prediction and the experimental results was achieved. This confirms the capability of the computer simulation and the used program for modeling heterostructures for application as band pass filters and antireflection coatings.

4. Conclusions

This study is based on the combination of first principals calculations and characteristic matrix theory. The optical properties (optical dielectric function, refractive
index and extinction coefficient) of rutile-TiO$_2$ (as a high reflective index (H) material) and α-Al$_2$O$_3$ (as a low refractive index (L) material) were studied using the full potential linearized augmented plane wave method. This study shows that our model (DFT + characteristic matrix) is a powerful method for theoretical analysis of optical properties of heterostructures. Different 15-fold samples were proposed and their transmittance spectra were depicted in various diagrams. We summarize our results as follows:

Stacks of high and low index materials can be used in order to make filters. The number of layers and the thickness of them should be considered in making a multilayer filter. We have shown that there is a linear relation between $\lambda_{NBPP}$ and the thickness of 8th layer but the growth rate of $\lambda_{NBPP}$ for first three samples (where the thicknesses of TiO$_2$ layers are smaller) is faster. This study also shows that the $\lambda_{NBPP}$ increases with the number of layers, the thickness of layers (especially, thickness of TiO$_2$ layers) and the thickness of 8th layer. It should be noted that our results are in good agreement with the experimental reports and we can rely on this model as a powerful method for studying optical behavior of heterostructures. We have shown that different samples can be combined in order to make a proper filter at desired positions of spectra. However, the proposed model is very flexible and the effect of many parameters such as thicknesses, incident angle, light polarization and arrangement of layers can be easily investigated.

References

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