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Fabrication of absorbing Nb-Ti suboxide anti-reflective thin film stacks

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ABSTRACT

Optically black anti-reflective coatings that absorb light are potentially useful for color isolation in the flat panel display industries and stray light reduction in imaging technologies. Here we report the design and fabrication of high performance multilayered black anti-reflective coatings. Thin film suboxides $Nb_xTi_{1-x}O_2$, NbO_2 and TiO_{2-x} were prepared using pulsed laser deposition (PLD). Their optical constants were then used to design a six layer coating which has less than 2% reflectivity across the visible range (400–700 nm) even at moderate incidence angles. Furthermore, this six layer coating displays large and constant absorbance across the visible range making it optically black. This optical behavior is due largely to the use of the suboxide $Nb_xTi_{1-x}O_2$ which is unique because of its spectrally constant absorption coefficient.

Coatings with wavelength independent optical absorption, transmission and reflection are important for technologies such as imaging and flat panel displays [1]. In flat panel displays, contrast performance and light isolation are achieved by using a neutrally absorbing black matrix material [2]. The black matrix also dictates the powered-off appearance of the display. Ideally, the black matrix should absorb all visible wavelengths with constant intensity. Such neutrally absorbing materials are also important for stray light suppression in imaging technologies [3]. It is important for absorbing materials to have good anti-reflective properties in order to enhance their light isolation abilities. High performance anti-reflective coatings display luminous reflectivity less than several percent across their intended spectral range [4]. Additionally, their spectral reflectivity remains low even at high incidence angles.

We recently identified a thin film suboxide material, $Nb_xTi_{1-x}O_2$ that has an optical absorption coefficient that is nearly independent of incident light wavelength in the visible range [5]. This property is unique among semiconducting materials used for light absorption. For example, thin Si appears red because its absorption coefficient declines with increasing wavelength [6]. Thin film $Nb_xTi_{1-x}O_2$ appears optically black due to its wavelength independent absorption coefficient. It has both semiconducting and metallic optical bands giving rise to its unique absorption behavior [5]. Although $Nb_xTi_{1-x}O_2$ has an optically black appearance well suited for light isolation applications, thin films prepared using pulsed laser deposition (PLD) have high reflectivity around 30% even at moderate incidence angles due to their high refractive index of 2.49 at 550 nm. Such high reflectivity is undesirable for imaging and display applications.

Here we report on the integration of $Nb_xTi_{1-x}O_2$ and two related suboxides NbO_2 and TiO_{2-x} into anti-reflective multilayers. We fabricated two multilayers: a four layer and a six layer. The suboxides, NbO_2, TiO_{2-x} and $Nb_xTi_{1-x}O_2$ were used as high refractive index layers. The low refractive index layers were SiO_xN_y also deposited by PLD [7]. The six layer coating displayed average reflectivity around 1.5% across the visible range (400–700 nm) while maintaining a black appearance with spectrally independent absorption. Periodic surface morphologies have been used to achieve broadband anti-reflection properties [8–10]. However, fabrication of these patterned surfaces is often complex and time consuming therefore our approach utilizes the smooth surfaces produced by PLD.

In general, for oxide PLD under oxygen rich conditions, films are very similar in composition and oxygen stoichiometry to the bulk targets used for their deposition. It has been shown that fully stoichiometric TiO_2 [7,11,12], Nb_2O_5 [13] and $TiNb_2O_7$ [14–16] films deposited by PLD are optically transparent when deposited under sufficient P_{O2}. However, there has been little investigation of the Nb-Ti-O system deposited by PLD under the oxygen deficient conditions of a vacuum. We found previously that PLD deposition in a vacuum using TiO_2, Nb_2O_5 and $TiNb_2O_7$ targets yielded the suboxide phases TiO_{2-x}, NbO_2 and rutile $Nb_xTi_{1-x}O_2$, respectively [5]. EDS indicates our $Nb_xTi_{1-x}O_2$ films have $x = 0.71$. The suboxide films are partially transparent with varying degrees of black coloration. It should be noted that TiO_2 suboxide 'Magnélí' phases have complex structures and stoichiometries [17]. A phase study of our TiO_2 suboxide films related them

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most closely to Ti_4O_7 but we will refer to them as TiO_{2-x} since they are amorphous with no regular ordering [5]. For the present study, we deposited monolithic films in a vacuum $\sim 1 \times 10^{-5}$ Pa on room temperature and 600 °C alkali-free glass substrates (OA-10, 15 mm × 15 mm × 0.5 mm, Nippon Electric Glass Co., Ltd.) in order to obtain temperature dependent optical properties, phase information and growth rates. Films deposited on substrates heated to 600 °C showed moderate crystallinity while films deposited at room temperature were amorphous [5]. We used a KrF excimer laser (λ = 248 nm) repeating at 5 Hz and a laser fluence of 5.8 J cm^{-2}. Growth rates did not vary drastically with temperature and were around 1–3 nm/min for all compositions. The SiO_xN_y films used for low index layers in the multilayers were deposited using a Si_3N_4 target with the same laser parameters stated above in an atmosphere with a constant P_{O2} of 5 Pa. The growth rate of SiO_xN_y was ~10 nm/min.

Sufficient levels of oxygen vacancies shift the cationic valencies of Nb and Ti, resulting in partially metallic phases that strongly absorb visible light. Crystallinity influences both the magnitude and spectral uniformity of the suboxide absorption coefficients. This effect is likely due to temperature dependent oxygen deficiency and cationic coordination [5,18]. We obtained refractive index, n, extinction coefficient, k and thicknesses of our monolithic films using spectroscopic ellipsometry. Absorption coefficients were derived from the optical constants. The effect of substrate temperature during deposition on absorption coefficient is illustrated for $Nb_xTi_{1-x}O_2$, NbO_2 and TiO_{2-x} PLD thin films in Fig. 1a, b and c, respectively.

To design the anti-reflection stacks, we input our measured wavelength dependent n and k values into the IMD [19] software package. By defining a target reflectivity profile and a stack of thin film layers, IMD assigns thicknesses within a defined range to layers in the stack and solves the Fresnel equations for that set of thicknesses. The calculated reflectivity of the stack is then compared to the user defined target profile and the set of thicknesses is given a figure of merit. IMD optimizes layer thicknesses for the user-defined stack such that the target reflectivity profile is closely matched. The optimization is based off a genetic algorithm wherein a starting population of stacks with varying layer thicknesses is randomly mutated until an individual with a satisfactory figure of merit is found [20]. This genetic modeling technique is extremely useful for the design of functional optical coatings. In our case, we fabricated several absorbing anti-reflective coatings designed with this method and verified that optical performance predicted by the model matches reality reasonably well.

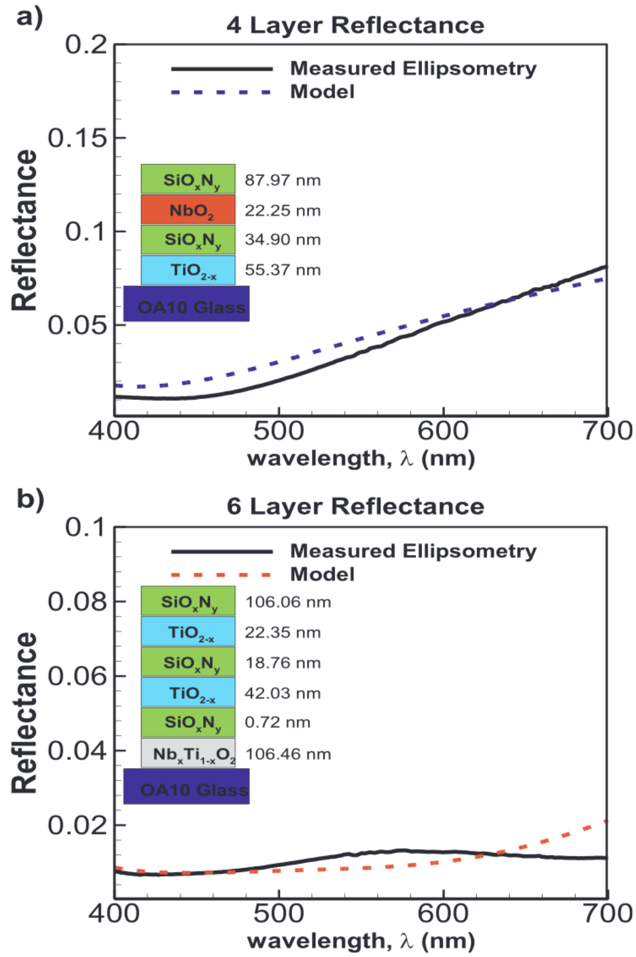
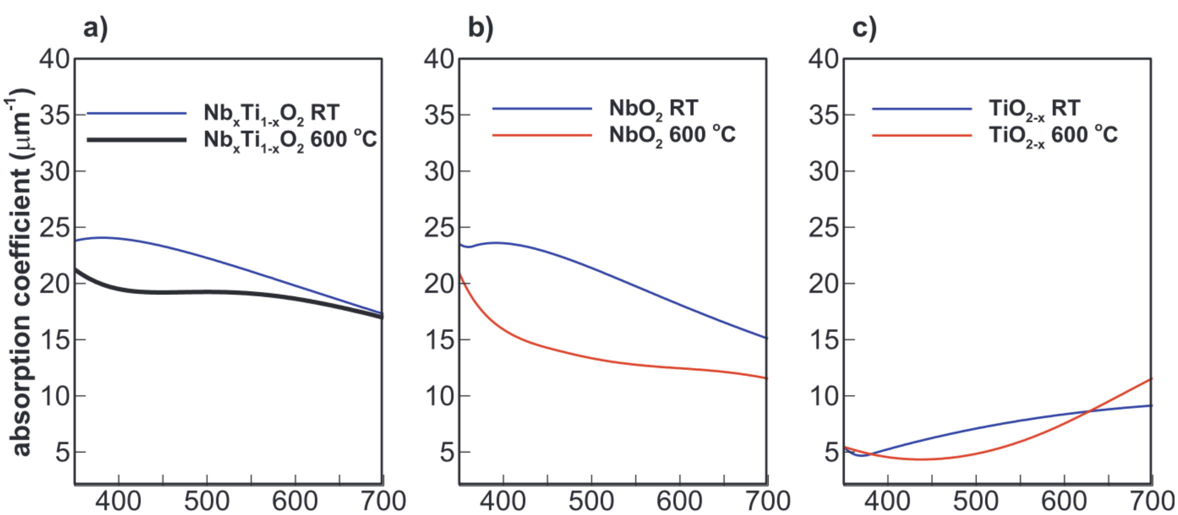


Fig. 2. Modelled and ellipsometrically measured reflection spectra at 50° incidence of a) the four layer stack and b) the six layer stack. Schematically shown are their constituent film make-ups and their measured thicknesses.



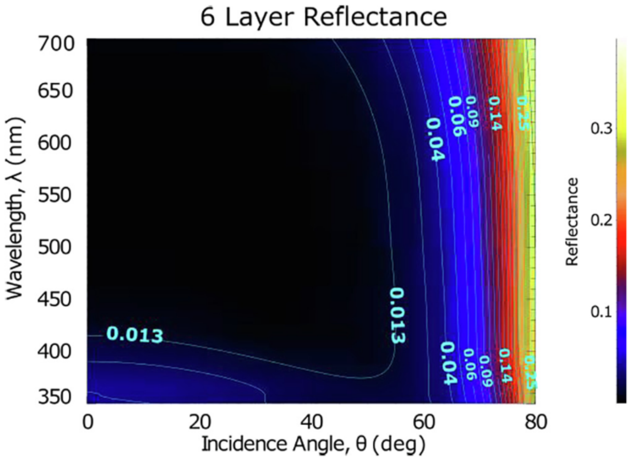


Fig. 3. Reflection contour plot generated from the modelled six layer data.

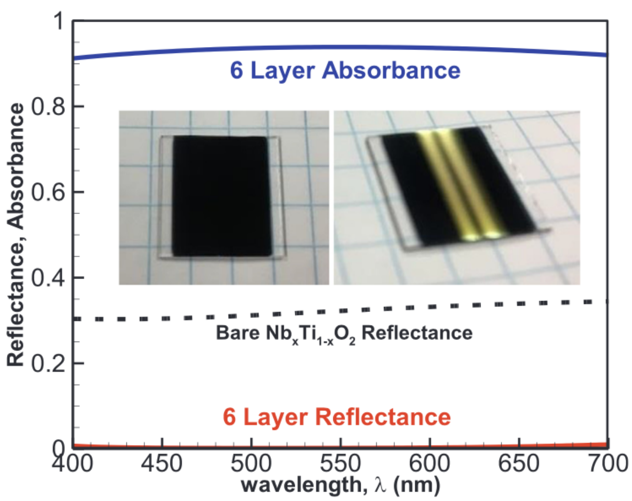


Fig. 4. Reflectance at 50° incidence and absorbance spectra of the six layer stack and reflectance of a bare $Nb_xTi_{1-x}O_2$ film. Inset are pictures of the six layer at normal incidence (left) and ~60° incidence (right). A specular reflection from overhead lights is in the visible right image.

We first fabricated a four layer anti-reflective stack using NbO_2 and TiO_{2-x} as the high index layers and SiO_xN_y [7] as the low index layers. All layers were deposited at room temperature. A schematic diagram of both composition and measured layer thicknesses is shown in Fig. 2. Adjusting the model to the measured thicknesses yields the dashed line in Fig. 2a. The adjusted model is in good agreement with the actual reflectance measured by ellipsometry. The ellipsometry measurements in Fig. 2 were taken at 50° incidence and the model line was calculated for 50° incidence. TiO_{2-x} absorbs strongly in the 550–700 nm range while NbO_2 absorbs strongly in 400–550 nm range as seen in Fig. 1b and c, respectively. A specific thickness ratio of about 5:2 for TiO_{2-x}:NbO_2 was used in the four layer stack in order to achieve constant absorption at all visible wavelengths. However, this thickness ratio constraint resulted in an inconsistent spectral reflectance profile.

Our six layer stack used $Nb_xTi_{1-x}O_2$ and TiO_{2-x} as the high index layers and again SiO_xN_y as the low index layers. The $Nb_xTi_{1-x}O_2$ was deposited at 600 °C while the subsequent layers were deposited at room temperature. The six layer showed excellent anti-reflection and absorption properties compared to the four layer. It is known that anti- of the $Nb_xTi_{1-x}O_2$ layer. Its use rather than NbO_2 removed the thickness ratio constraint between the high index layers. The six layer reflectance profile is shown in Fig. 2b. Again, the model was adjusted to reflect measured layer thicknesses after deposition; it is in good agreement with the measured data. The model was then extrapolated to simulate the six layer stack's performance at incidence angles from 0 to 80° as shown in Fig. 3.

This six layer anti-reflective coating shows excellent performance with reflectance below 2% across the visible range (400–700 nm) even at fairly large incidence angles. Along with wavelength and incidence angle reflectance, we are able to simulate film stack absorbance using the model. The model uses the relationship $A + T + R = 1$. Our six layer coating is still slightly transparent which is potentially useful for light filter type applications. Although transmittance can certainly be brought to zero by increasing the absorbing layer thicknesses. Compared to bare $Nb_xTi_{1-x}O_2$, the six layer stack has drastically reduced reflectance as shown in Fig. 4.

Our suboxide absorbing anti-reflective coatings achieve excellent broadband anti-reflective and absorbing properties without the use of surface morphology. To our knowledge, this is the first use of Nb and Ti suboxides for high performance anti-reflective and absorbing optical coatings. The suboxide $Nb_xTi_{1-x}O_2$ is especially well suited for integration into absorbing anti-reflective film stacks because of its nearly constant absorption coefficient which results in a spectrally black appearance. We obtained optical constants n and k of single PLD films on glass using spectroscopic ellipsometry. This data coupled with genetic optimization software drove the design of multilayer stacked coatings. After fabrication, we measured the thicknesses of individual layers in the coatings and modelled their overall optical performance. Suboxide materials have enormous potential for optical applications. Their transmission, absorption and reflection properties can be manipulated by varying oxygen content. Applying suboxide layers to multilayer coating design is not limited to broadband anti-reflective coatings. Narrow band and more exotic absorption and reflection properties can certainly be realized in suboxide coatings with the use of genetic modelling software.

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