Compositional dependence of absorption coefficient and band-gap for Nb_2O_5-SiO_2 mixture thin films

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Abstract

The absorption coefficient of composite films consisting of niobia (Nb_2O_5) and silica (SiO_2) mixtures is studied for photon energies around the band gap. The films were deposited by co-evaporation and their composition was varied by changing the ratio of deposition rates of the two materials. Both, as-deposited and thermally annealed films were characterized by different techniques: the absorption coefficient was determined by spectrophotometric measurements and the structural properties were investigated using infrared spectroscopy, transmission electron microscopy and X-ray diffraction. The correlation between the variations of absorption properties and film composition and structure is established. The absorption coefficients determined experimentally are compared with the results derived from effective medium theories in order to evaluate the suitability of these theories for the studied composites.

Keywords: composite thin films, effective medium theory, optical coatings, absorption coefficient

1. Introduction

Composite thin films consisting of the mixture of two or more materials have a wide range of applications. In the field of optical coating technology, the possibility to tailor the refractive index of materials is very attractive and has motivated the development of structures like gradient

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refractive index coatings [1]. These coatings have a continuous variation of the refractive index through the thickness, that can be achieved by modifying the mixture composition during the deposition. Due to the absence of interfaces, gradient refractive index coatings present particular advantages with respect to the classical multilayer stacks, like reduced scattering losses, better mechanical properties [2,3] and higher resistance against radiation [4]. At the same time, designs of gradient refractive index coatings have optical spectral performances comparable or superior to designs of classical coatings [5].

The modification of optical properties of a mixture with the composition affects not only the refractive index but also the absorption coefficient. The precise knowledge of the compositional dependence of refractive index is essential for the design of coatings with required performance and, consequently, has been focus of extensive research [6]. Also, knowing the compositional dependence of the absorption edge is necessary to define the spectral range where mixtures are transparent and thus useful for optical coatings in which absorption must be avoided. Additionally, the determination of very small values of absorption coefficient, like for energies below the band gap, may be also desirable as it is correlated with the radiation resistance of coatings [7]. The most usual way to compute the optical constants of mixtures is using effective medium theories, that calculate effective optical constants in terms of the optical constants and volume fractions of the composing materials [8]. Although these theories have been successfully applied to model the compositional dependence of the refractive index in thin films [9,10] their suitability for the absorption coefficient determination is generally overlooked.

In the present work the compositional dependence of the absorption coefficient for energies around the band gap for Nb_2O_5-SiO_2 thin film mixtures has been analyzed. The results of optical and structural characterization of as-deposited and annealed samples show the correlation between the absorption coefficient and structural properties of the mixtures. Finally, the comparison between experimental data and calculations from classical effective medium theories evidences the limitations of these theories to describe the compositional dependence of the absorption coefficients of the studied mixtures.

2. Experimental

A set of Nb_2O_5-SiO_2 mixture layers was deposited on fused silica (Suprasil) substrates by co-evaporation in a Leybold Syrius Pro 1100 system equipped with two electron beam guns and Advanced Plasma Source [11]. This combination of materials has been used for the design [12] and deposition [13] of inhomogeneous coatings for antireflection purposes. The volume fraction of mixing materials was controlled by adjusting the deposition rates. Mixtures containing Nb_2O_5:SiO_2 volume ratios of 80:20, 65:35, 50:50, 35:65 and 20:80 were produced. Single layers of the pure materials were also deposited. Layer thickness was about 500 nm. The samples were studied as-deposited and also after five hours of annealing at 750° C.

Reflectance and transmittance measurements at normal incidence were performed in the spectral range between 200 and 900 nm with a Perkin Elmer Lambda 900 spectrophotometer. The absorption coefficient was determined by direct inversion of the experimental measurements. According to the thickness of layers and the measurements accuracy, the absorption coefficient could be determined for values down to approximately 10^2 cm^{-1}. Additionally, structural characterization was carried out using different techniques: X-ray diffraction, transmission electron microscopy and infrared spectroscopy. The details of structural characterization techniques and results will be reported elsewhere.

3. Results

All the deposited layers, except the pure SiO_2, show an absorption edge in the UV part of the spectra. The edge is shifted towards higher photon energies as the amount of SiO_2 in the mixture increases. The absorption edge of the annealed composites is shifted towards lower photon energies with respect to the as-deposited composites. Absorption of pure Nb_2O_5 layer after annealing could not be determined due to the high scattering losses. A more detailed analysis reveals that two different absorption ranges can be distinguished in the absorption edges of the composites. As first, at lower energies, a linear dependence of the logarithm of the absorption coefficient (α) with the energy (E) is identified, as shown in Fig. 1. This dependence is related to transitions between extended and localized states [14], typically modelled by the Urbach expression [15]:

$$\alpha(E) = \alpha_0 \exp\left(E \big/ E_0 \right), \tag{1}$$

where α_0 is a constant and E_0 is the so-called Urbach energy, interpreted as the width of the tail of localized states in the forbidden band gap and usually associated to structural and thermal disorder. Only the composite with 80:20 ratio did not show this linear dependence after annealing, most likely due to scattering losses that masked small absorption levels. The second absorption range of the composites is found at higher energies, where the absorption is related to electronic interband transitions. For a large number of materials, the energy dependence of the absorption coefficient associated to these transitions has been successfully described by [16]:

$$\alpha(E) = C(E - E_g)^n \big/ E, \tag{2}$$

where C is a parameters related to the optical transition matrix and E_g is the Tauc gap, defined as the energy separation between valence and conduction band and representing the onset of absorption related to interband transitions. The exponent n equals to 1/2 for direct transitions and to 2 for indirect transitions. For the studied composites, n=2 describes the experimental data better, in accordance with other results reported for oxide mixtures [17]. In Fig. 2 the Tauc plots, i.e. $(\alpha E)^{1/2}$ versus E, are represented, supporting the validity of Eq. 2. The parameters describing the absorption coefficient in the studied spectral range (α_0, E_0, C and E_g) have been determined by least square fits of the experimental to Eqs. 1 and 2. The parameter values for all samples are summarized in Table 1.

In order to examine the capacity of effective medium theories for describing the absorption behaviour of these composites, the Bruggeman [18] and Lorentz-Lorenz [19] models have been used. These two models have been chosen since they appeared to be the most successful for describing the compositional dependence of the refractive index in oxide mixtures films [9,10] and are among the most frequently used. The expressions for the effective dielectric function (ε_{eff}) reads as:

$$\frac{\varepsilon_{eff}-1}{\varepsilon_{eff}+2}=f\,\frac{\varepsilon_1-1}{\varepsilon_1+2}+\;1-f\;\;\frac{\varepsilon_2-1}{\varepsilon_2+2}\,, \tag{3}$$

for the Lorentz-Lorenz model and

$$f\,\frac{\varepsilon_1-\varepsilon_{eff}}{\varepsilon_1+2\varepsilon_{eff}}+(1-f)\,\frac{\varepsilon_2-\varepsilon_{eff}}{\varepsilon_2+2\varepsilon_{eff}}=0\,, \tag{4}$$

for the Bruggeman model. In these expressions ε_1 and ε_2 stand for dielectric functions of the composing materials and f and $1-f$ are their respective volume fractions. The absorption coefficient for each mixture has been computed according to these models using the optical constants of SiO_2 and Nb_2O_5 determined from measurements of the as-deposited pure material layers and the volume fractions estimated from the deposition rates. For the annealed samples such comparison was not possible since the optical constants of annealed Nb_2O_5 could not be determined as mentioned before. It has been found that for all the composites and photon energies the effective medium theories give absorption coefficients higher than those observed experimentally. These discrepancies are more important for lower photon energies, while at higher energies the Lorentz-Lorenz model appears to be a fair approximation to the experimental data. A detailed comparison is shown in Fig. 3.

The structural characterization indicates that all the as-deposited samples are amorphous. Transmission electron microscopy (Fig. 4a) shows that no separated phases of Nb_2O_5 and SiO_2 can be identified according to the high degree of homogeneity of the mixture. This fact is supported by the results of infrared spectroscopy measurements that revealed the presence of an absorption band at 920 cm^{-1} that is attributed to the presence of Si-O-Nb bonds. After annealing, crystallisation of Nb_2O_5 in its orthogonal and hexagonal phases was observed from X-ray diffraction for those samples with higher content of Nb_2O_5 (pure Nb_2O_5, 80:20 and 65:35). The crystallisation of Nb_2O_5

has been confirmed by transmission electron microscopy images (Fig. 4b), where separation between SiO_2 and Nb_2O_5 phases was evidenced. This phase separation is supported by intensity reduction of the absorption band of Si-O-Nb bonds and increase of intensity of the absorption bands of Si-O-Si and Nb-O-Nb bonds in the infrared spectra.

4. Discussion

The study of the absorption coefficient of the composites shows the presence of absorption for energies below the band gap, obeying the Urbach law (Eq. 1). The parameter values in Table I indicate that the Urbach energy for the as-deposited samples is minimum for pure Nb_2O_5 and increases with the content of SiO_2 (typical values of E_0 for SiO_2 are around 0.15 eV [20]). The Urbach energy is frequently used to quantify the degree of structural disorder [21]. Therefore, since the as-deposited composites show an amorphous homogenous structure with SiO_2 and Nb_2O_5 mixed at molecular level, it is likely that the structural disorder varies monotonically from the disorder of pure Nb_2O_5 to the disorder of pure SiO_2. Such variation is supported by the compositional dependence of the Urbach energy. The situation is rather different for the annealed samples, where the values of the Urbach energy are higher and its compositional dependence is less remarkable compared to the as-deposited samples. The higher values of the Urbach energy can be attributed to the appearance of localized states associated to the grain boundaries, owing to the phase separation of materials. Due to this contribution, the correlation of the Urbach energy with the mixture composition and the structural disorder of the pure materials may be weaker to that observed for the as-deposited samples.

At higher energies, the absorption coefficient obeys the Tauc expression (Eq. 2). For both as-deposited and annealed samples, the value of the Tauc gap increases with the content of SiO_2. The Tauc gap defines the onset of absorption related to the interband transitions that can be associated to the presence of Nb_2O_5, since SiO_2 is transparent in the studied spectral range. For the as-deposited samples, Nb_2O_5 does not appear as a separated phase, but mixed at molecular level with SiO_2. Thus, the band structure of the material and, therefore, the absorption onset will be significantly different from that of pure Nb_2O_5. The situation is different for the annealed samples. Since the separation of Nb_2O_5 and SiO_2 phases occurs, the absorption onset should be closer to that of pure Nb_2O_5. For this reason, the variations of the Tauc gap with the composition are more remarkable for the as-deposited mixtures than for the annealed ones.

In order to analyze the failure of effective medium theories to describe the compositional dependence of the absorption coefficient properly, one has to take into account that for dielectric materials with low absorption levels, these theories essentially consist on an average of the optical constant of the composing materials [8]. Since SiO_2 is transparent, the absorption coefficient of the mixtures can be roughly approximated as the multiplication of the absorption coefficient of Nb_2O_5 by some factor. In the case of the Bruggeman model this factor is approximately the volume fraction, while for the Lorentz-Lorenz model is a smaller quantity. That can be clearly observed in Fig. 5, showing the calculations of effective medium theories in logarithmic scale, where the computed absorption edges of the mixtures appear to be nearly parallel. Therefore, these theories state that the energy range of validity of the Urbach and Tauc expressions for all mixtures is the one of pure Nb_2O_5, what is in contradiction with the experimental results. Consequently, the effective medium theories do not indicate a compositional dependence of the Urbach energy or the Tauc gap. These theories assume that mixture materials are present in the composite in separated phases, with typical individual sizes large enough to have their own electromagnetic behaviour. As the structural characterization indicated, this condition is not accomplished for the as-deposited samples. Nevertheless, the non achievement of this condition is more critical for modelling the absorption coefficient around the band gap, where it is strongly connected to the material microstructure, than for the refractive index, primarily associated to the material density. In this way, the success of effective medium theories for modelling the refractive index can be understood. In any case, from a qualitative point of view, the Lorentz-Lorenz model appears to describe the compositional dependence of the absorption edge better than the Bruggeman model, in connection with results reported for the compositional dependence of refractive indices of amorphous composites [10]. However, the validity of the Lorentz-Lorenz model can only be assessed for the highest energies of the studied spectral range, in which all the composites obey the Tauc expression.

5. Conclusions

The correlation between the absorption coefficient around the band gap with the composition and with the structural properties of Nb_2O_5-SiO_2 mixtures has been studied. Spectral ranges where the absorption obeys the Urbach law and the Tauc expression have been found for as-deposited and annealed samples. As-deposited samples show homogeneous amorphous mixtures of Nb_2O_5 and SiO_2 at molecular level. Correspondingly, the parameters describing the energy dependence of the absorption edge, like the Urbach energy and the Tauc gap, vary between the values of pure materials. Separation of Nb_2O_5 and SiO_2 phases due to thermal annealing is observed. In this case, the compositional dependence of the mentioned parameters is weaker. Effective medium theories fail to describe the absorption properties in most of the spectral range of interest, since these theories do not show a compositional dependence of the Urbach energy and Tauc gap parameters.

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List of Table captions

Table 1 - Structural parameters describing the energy dependence of the absorption coefficient. Parameters corresponding to annealed pure Nb_2O_5 and α_0 and E_0 of annealed 80:20 mixture could not be determined due to high scattering losses.

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Fig. 1 - Energy dependence of the absorption coefficient of the as-deposited (a) and annealed (b) mixtures. Solid lines illustrates the validity of the Urbach law.

Fig. 2 - Tauc plots of the as-deposited (a) and annealed (b) mixtures. Solid lines illustrate the validity of the Tauc expression.

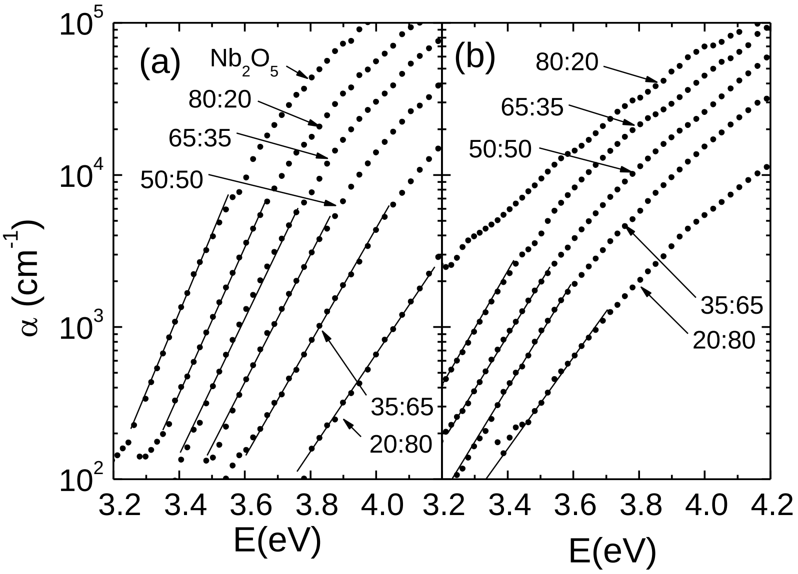
Fig. 3 - Compositional dependence of the absorption coefficient at different energies: experimental (dots) and computed according to Bruggeman (solid lines) and Lorentz-Lorenz (dashed lines) models.

Fig. 4 - Cross section transmission electron microscopy of the 80:20 mixture: as-deposited (a) and annealed (b)

Fig. 5 - Energy dependence of the absorption coefficient calculated according to the Bruggeman (a) and Lorentz-Lorenz (b) models.

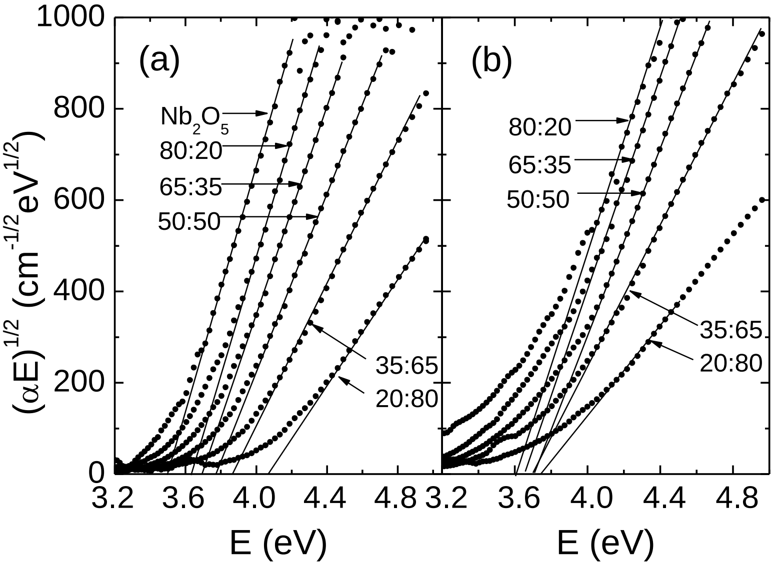
Sample	As deposited				Annealed			
	α_0 (cm^{-1})	E_0 (eV)	C(cm^{-1}eV^{-1})	E_g (eV)	α_0 (cm^{-1})	E_0 (eV)	C(cm^{-1}eV^{-1})	E_g (eV)
20:80	$4.91\cdot10^{-11}$	0.132	567	4.09	$4.00\cdot10^{-10}$	0.127	499	3.75
35:65	$7.53\cdot10^{-12}$	0.117	782	3.87	$3.26\cdot10^{-11}$	0.112	771	3.71
50:50	$4.62\cdot10^{-13}$	0.104	987	3.78	$1.15\cdot10^{-9}$	0.124	1038	3.70
65:35	$5.21\cdot10^{-14}$	0.096	1148	3.70	$1.59\cdot10^{-9}$	0.121	1186	3.67
80:20	$1.62\cdot10^{-14}$	0.090	1240	3.61	-	-	1220	3.60
Nb_2O_5	$9.75\cdot10^{-16}$	0.082	1332	3.49	-	-	-	-

Table 1



(a)
(b)
Nb$_2$O$_5$
80:20
65:35
50:50
35:65
20:80
α (cm^{-1})
10^2
10^3
10^4
10^5
3.2
3.4
3.6
3.8
4.0
4.2
E(eV)

Fig. 1



(a)
(b)
Nb$_2$O$_5$
80:20
65:35
50:50
35:65
20:80
$(\alpha E)^{1/2}$ (cm$^{-1/2}$eV$^{1/2}$)
0
200
400
600
800
1000
3.2
3.6
4.0
4.4
4.8
E (eV)

Fig. 2

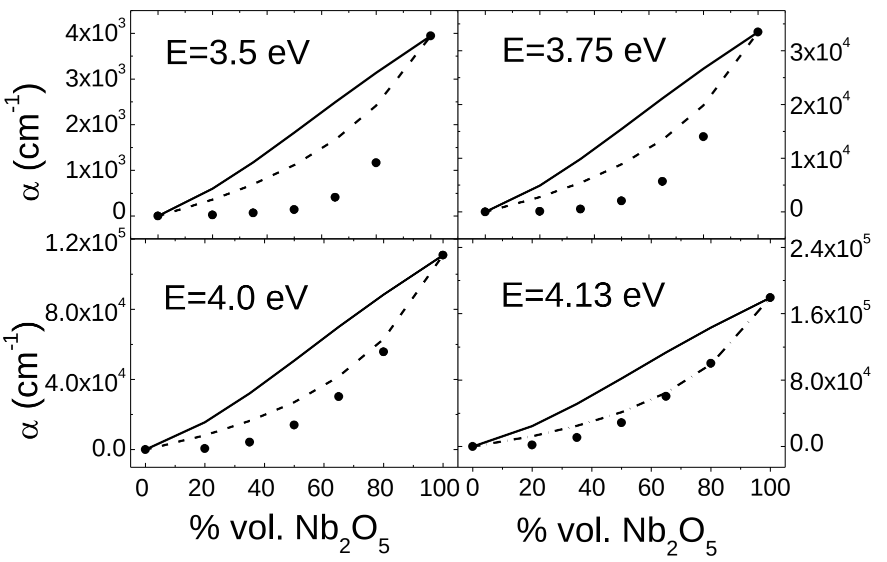

E=3.5 eV
E=3.75 eV
E=4.0 eV
E=4.13 eV
α (cm^{-1})
α (cm^{-1})
0
1x10^3
2x10^3
3x10^3
4x10^3
0
1x10^4
2x10^4
3x10^4
0.0
4.0x10^4
8.0x10^4
1.2x10^5
0.0
8.0x10^4
1.6x10^5
2.4x10^5
0
20
40
60
80
100
% vol. Nb$_2$O$_5$
% vol. Nb$_2$O$_5$

Fig. 3

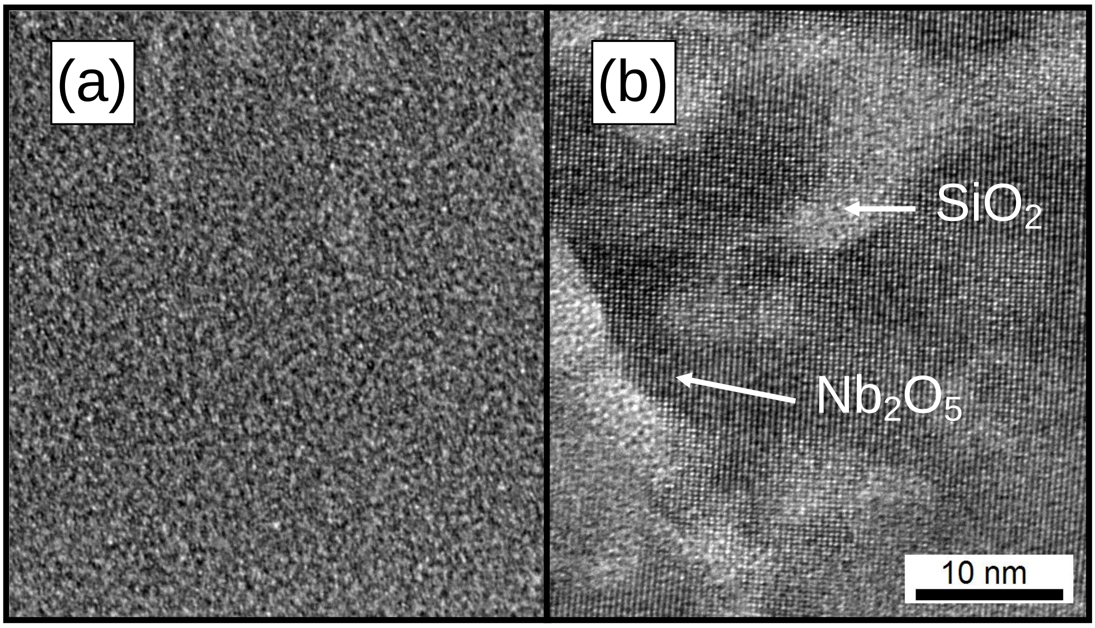

(a)
(b)
SiO$_2$
Nb$_2$O$_5$
10 nm

Fig. 4

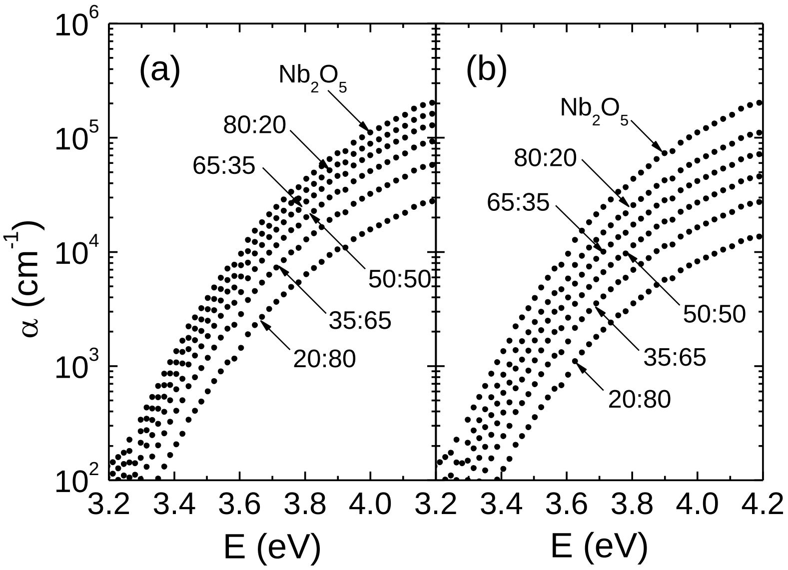

(a)
(b)
Nb2O5
80:20
65:35
50:50
35:65
20:80
α (cm-1)
E (eV)
10^6
10^5
10^4
10^3
10^2
3.2
3.4
3.6
3.8
4.0
4.2

Fig. 5