Temperature dependence of the 4-eV optical transition in $YBa_2Cu_3O_6$

Marcel E. Bijlsma,* Herbert Wormeester,† Dave H. A. Blank, Edward Span, Arend van Silfhout, and Horst Rogalla
Department of Applied Physics, Centre for Materials Research, University of Twente,
P.O. Box 217, 7500 AE, Enschede, The Netherlands
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With spectroscopic ellipsometry the optical properties of high quality $YBa_2Cu_3O_6$ thin films deposited by off-axis magnetron sputtering were investigated *in situ*. The optical transition at 4 eV of these films that were not exposed to atmospheric condition shows a two times higher magnitude than reported previously and can be described by a single Lorentz oscillator in the complete temperature range of 20 °C–700 °C. The width of the Lorentz oscillator is remarkably small. Combined with the temperature-independent strength of one electron per unit cell of the 4-eV transition, it is an indication that this optical transition takes place between a quite isolated occupied and unoccupied level of the electronic structure. [S0163-1829(98)01722-6]

The nature of electronic states in high-T_c superconducting materials plays a key role in the understanding of both the normal-state properties and the superconducting mechanism in these materials. For the $YBa_2Cu_3O_{7-\delta}$ compound, where δ can range between 0 and 1, its (super)conducting behavior diminishes with increasing δ, resulting in a semiconducting behavior for $\delta > 0.6$. The strong dependence of the electronic band structure, as represented by the complex dielectric function, on the oxygen content in these cuprate materials has a drastic effect on the visible-near UV optical response of the material. Therefore, using spectroscopic ellipsometry in this energy region, we can probe changes in the dielectric function and relate indirectly the optical response to the oxygen content in the $YBa_2Cu_3O_{7-\delta}$ thin films.

Several *ex situ* ellipsometric studies on the $YBa_2Cu_3O_{7-\delta}$ compound (mostly on single crystals) reveal an electronic transition band centered around an energy of 4.05 eV, whose strength decreases with increasing oxygen content.[1–8] In this study on sputter-deposited c-axis-oriented $YBa_2Cu_3O_{7-\delta}$ thin films, we investigate *in situ* and directly after deposition the temperature dependence of the visible-NUV complex dielectric function in the limiting case where $\delta = 1$ (tetragonal phase) and the transition band strength is maximum. Investigation of the temperature dependence of the dielectric function $\varepsilon(E)$, especially in the neighborhood of interband critical points (CP's), can give us interesting information on the coupling of the electronic transitions to low-energy excitations.[9,10] In contrast to metallic $YBa_2Cu_3O_7$, for which the temperature dependence of $\varepsilon(E)$ has been studied in detail (Ref. 11 and references therein), very few papers are devoted to the analysis of the CP behavior in the nonmetallic state. An important reason is the failure of (one-electron) band-structure calculations to describe the low-oxygen content $YBa_2Cu_3O_6$ phase. As a result, a direct coupling between experiment and the electronic band structure is not yet possible. Nevertheless, earlier studies on the 4-eV transition attribute this CP to transitions localized in the chain Cu-O subsystem.[5,6] Oxygen ordering in the Cu-O chain plane can be observed by studying the change in the 4-eV transition.[12,13] As a result, the amplitude of the imaginary part of the dielectric function at the CP scales with the actual oxygen content in the compound. The dimensionality of the CP, characterized by the (temperature-dependent) line shape of the CP, has been subject of two studies. Humlicek and co-workers[7] in an early study on $YBa_2Cu_3O_6$ single crystals found a Lorentzian oscillatorlike line shape. In contrast, Boyn *et al.*[14] analyze the optical response of epitaxial thin films using a Gaussian line shape to describe the CP line shape in the temperature-range of -200 °C to 500 °C. To solve this ambiguity, we performed a temperature-dependent line-shape analysis on the dielectric function near the 4-eV CP in the 20 °C to 700 °C temperature range.

All experiments are performed *in situ* directly after off-axis magnetron sputter deposition of nominally 200 nm-thick thin films on standard single crystalline (001) $SrTiO_3$ substrates. Due to our *in situ* measurement ability, formation of any surface interface layer with probable degraded properties, which will influence the optical response, is prevented. All films are deposited under optimal deposition conditions, i.e., a deposition temperature of $T_{dep} = 770$ °C, a total sputter pressure of $P_{tot} = 0.20$ mbar, an Ar: O_2 gas ratio of 3:4 and a sputter power of $P_{rf} = 90$ W resulting in completely c-axis textured thin films, as determined by x-ray diffraction (XRD). Details can be found elsewhere.[15] To reach the $YBa_2Cu_3O_6$ phase, no additional oxygen annealing step was carried out, but instead the thin films were annealed at low oxygen pressure at high temperature to remove oxygen introduced into the lattice during the deposition process. The thin-film oxygen content was indirectly deduced by the combination of the measurement of the c-axis length as determined by *ex situ* XRD and the amount of decrease of superconducting transition temperature T_c with respect to the fully oxygenated thin-film value. Fully oxygenated samples showed a T_c in the order of 89.6 ± 0.4 K. Critical current-density values were around $j_c = 2 \times 10^6$ A/cm^2 at 77 K.

Ellipsometric measurements were performed using a homebuilt rotating polarizer-sample-analyzer ($P_{rot}SA$) configuration with a 75 W Xe lightsource. Our multichannel detector consists of an Oriel multispec sprectrograph with a 300 l/mm grating in combination with an EG&G Reticon T series 256 pixel photodiode array. The spectrograph/array combination results in a bandpass on the detector of 325 nm. Using a stepping motor attached to the spectrograph a spectral response range of 200–1000 nm (1.5–5 eV) is feasible.

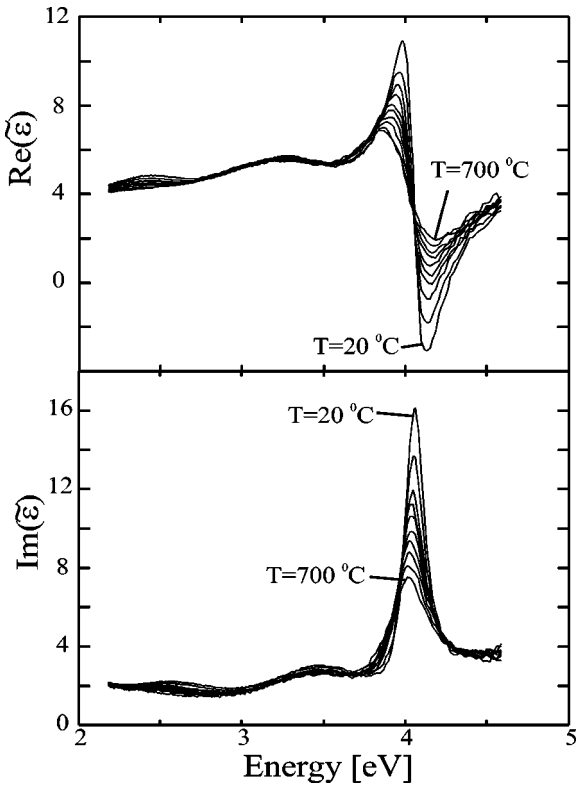

FIG. 1. Temperature dependence of $\langle\tilde{\epsilon}\rangle$ for $YBa_2Cu_3O_6$. Temperatures are (top-to-bottom) 700, 600, 500, 400, 350, 300, 250, 200, 85, and 20 °C, respectively, for both panels.

The angle of incidence is in all cases close to 70° and can be reproduced with a resolution of 0.05°. Details of the setup can be found elsewhere[15].

The measurement of the optical response was started at a high substrate temperature ($T=700$ °C) with a subsequent ramping down to lower temperatures. This prevents further oxygen loss at the lower temperatures. *Ex situ* conductivity measurements on these as-deposited films without any oxygen post-annealing treatment show the expected increasing resistance behavior with decreasing temperature. The *c*-axis value at room temperature was 1.191 ± 0.002 nm, which is indicative of a δ value very close to one.[18] The ellipsometric parameters $\tan(\Psi)$-$\cos(\Delta)$ were measured after the temperature had stabilized at the desired set point. These parameters were converted to an average complex pseudodielectric function form $\langle\tilde{\varepsilon}\rangle$. Anisotropic effects, which are intrinsical to the $YBa_2Cu_3O_6$ uniaxial crystal structure, can safely be neglected because in our case of nearly 100% textured *c*-axis oriented thin films, only the tensor element in the *a*-axis direction (lying along the line spanned by the plane of incidence and the $YBa_2Cu_3O_6$ surface) is probed.[16,17] The temperature dependence of $\langle\tilde{\varepsilon}\rangle$ for the very low-oxygen content films ($\delta=1$) is depicted in Fig. 1. The two Kramers-Kronig correlated spectra are dominated by three features, which are labeled CP0, CP1, and CP2. First, the sharp CP0 feature at 4 eV shows a strong dependence on temperature. With decreasing temperature the peak amplitude increases substantially and in addition an energy shift to higher energies can be observed. A second broad optical feature is visible near 3.5 eV (CP1). The amplitude of this shoulder structure does nearly not depend on temperature. Also it does not shift in energy. Finally, with decreasing temperature a third, much smaller, structure in the spectra can be seen to develop at an energy of 2.7 eV (CP2).

The amplitude of the imaginary part of the dieletric function at the CP0 reaches 16 at room temperature. This value is extremely high compared to all available literature, where at maximum a value of 8 can be found.[5] Moreover, data taken from samples that have been in contact with air for several days show a much lower excitation amplitude, comparable with literature values. The electrical properties of the air exposed samples were nevertheless not degraded. The difference in transition amplitude between our results and the literature is due to the high quality of our highly textured thin films in combination with our unique *in situ* measurement capability, which prevents any surface effects. The probe depth of ellipsometry is limited to several nm for the strong absorbing material under study. Thus only the outer unit-cell layers are measured, which have not been exposed to air in our experiments. The electrical properties are averaged over the whole thin film and are not likely to be influenced by a degradation of the top layer. Therefore, the claim of using *ex situ* optical measurements in the UV region to determine the actual oxygen content of high-T_c material samples from the amplitude of dielectric function spectra[8] needs, unfortunately, to be revisited. The relation between amplitude and oxygen content will only hold for measurements at comparable samples with similar electronic and microstructural properties and no general phenomenological relation holds. For $\delta=0$, the height of CP0 is determined by the amount of tetragonal oriented material in the depth range probed with ellipsometry, in relation to the amount of deformed unit cells induced by surface roughness, defects, etc. Especially, surface roughness can have a profound influence on the strength of the CP0 feature.

The temperature induced changes of the CP can be analyzed by describing the CP with standard analytic line shapes:[19]

$$\tilde{\varepsilon}(E)=C-A\ e^{i\varphi}\ (E-E_0+i\Gamma)^n,$$

where A represents the dimensionless amplitude (strength) of the transition, E_0 the threshold energy, Γ the line-shape broadening, and φ the excitonic phase angle. The exponent n has the value $-\frac{1}{2}$ for a one-dimensional transition, $n=0$ for two-dimensional (2D) [i.e., logarithmic: $\tilde{\varepsilon}(E)\sim\ln(E-E_0+i)$] and $\frac{1}{2}$ for 3D CP's. Discrete excitons, i.e., single Lorentz oscillatorlike, are described by an exponent $n=-1$. The 4-eV transition band structure is clearly superimposed on an energy-dependent background. Therefore, a least-squares fit procedure of the line shape on the first and second derivatives of $\tilde{\varepsilon}(E)$ with respect to E is performed. Both real and imaginary parts of the corresponding numerically differentiated measured pseudodielectric function $\langle\tilde{\varepsilon}\rangle$ were considered. We find that the 4-eV CP can be described with a Lorentz line shape ($n=-1$) over the whole investigated temperature range and that in all cases $\varphi=0$, implying that the line shape corresponds to transitions between uncorrelated one-electron bands, i.e.,

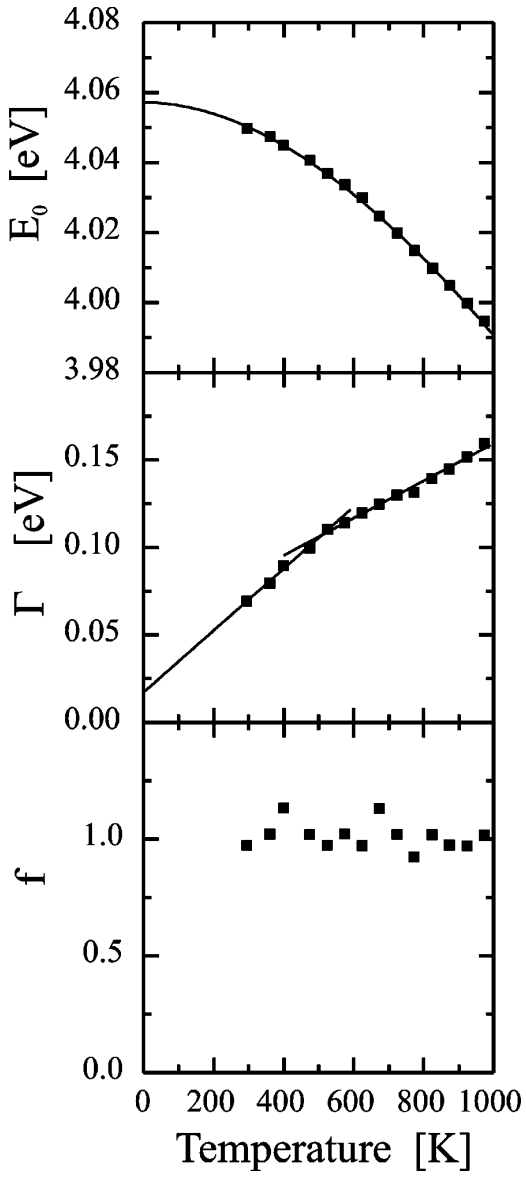

FIG. 2. Temperature dependence of the Lorentz oscillator parameters. (a) threshold energy of the CP0 critical point in $YBa_2Cu_3O_6$, (b) broadening parameter, and (c) oscillator strength.

$$\tilde{\varepsilon}(E)=C-\frac{\hbar^2}{2m\varepsilon_0 VE_0}\frac{f}{(E-E_0+i\Gamma)}.$$

In this, f is the oscillator strength, indicating the number of electrons per volume of the unti cell V involved in the optical transition. Both real and imaginary parts of $\langle\tilde{\varepsilon}\rangle$ were used, in contrast to Boyn *et al.*,[14] who fitted a phenomenological Gaussian peak on the imaginary part of $\langle\tilde{\varepsilon}\rangle$ only. Best fit parameter values as a function of temperature are given in Fig. 2. We observe a slight red shift of the transition in the high-temperature region. The shift decreases with decreasing temperature. At low temperatures it can be expected that E_0 will saturate. The dashed line in Fig. 2(a) represents a fit according to the empirical Varshni equation[20] (with T in Kelvin)

$$E_0(T)=E_0(0)-\frac{\alpha T^2}{T+\beta},$$

with $E_0(0)=4.057\pm0.005$ eV, $\alpha=(3.0\pm0.8)\times10^{-4}$ eV/K and $\beta=(3.5\pm1)\times10^3$ K. The inaccuracy of α and β is due to the almost linear temperature dependence in the experimental range. The value of $E_0(0)$ is model dependent, but also with a parabolic behavior it is within the error limits. The temperature-dependent energy shift is a combined effect of thermal lattice expansion and electron-phonon interaction. In this electron-phonon interaction mechanism, self-energy terms are likely to contribute to the energy shifts. Quantitative theoretical shift predictions are dependent on details of the band structure and are unfortunately not available for $YBa_2Cu_3O_6$. These effects also account for the increase of the half-width Γ with increasing temperature [see Fig. 2(b)]. Electron-phonon scattering leads to a shortening of the lifetime of the electron states and consequently to an increased broadening with temperature. The half-width Γ can be described by two linear segments, showing a temperature dependence of $\partial\Gamma/\partial T=0.107\pm0.004$ meV/K in the high-temperature range and $\partial\Gamma/\partial T=0.177\pm0.008$ meV/K in the low-temperature range. The ranges cross around 500 K, the Neél temperature of $YBa_2Cu_3O_6$. This indicates a possible relation between the 4-eV optical transition and the antiferromagnetic character of $YBa_2Cu_3O_6$. Also Humlicek and co-workers[7] found an increasing broadening with temperature. The magnitude of their broadening parameter is considerably higher than our values. This behavior is likely to have its origin in the nature of their randomly oriented, multigrained single-crystal sample, where anisotropic effects cannot be neglected. Our line-shape analysis is performed at rather high temperatures, where thermal broadening can still obscure small structures within the envelope peak structure. However, the extrapolated value of Γ at 0 K has the very low value of $\Gamma(T=0\text{ K})=17$ meV indicating that the occupied and unoccupied levels involved in the CP0 transition show virtually no dispersion. Therefore, they are of a very localized nature.

The strength of the Lorentz oscillator f is, within scatter margins, insensitive to the temperature [see Fig. 2(c)] and has an average value of $f=1.01\pm0.06$. This indicates a strong transition between two virtually isolated states. Consequently, the amplitude (strength) of the transition is a direct measure of the actual oxygen content, i.e., the amount of tetragonal oriented material in the film as each tetragonal unit cell gives its own, independent, contribution. The high value of the oscillator strength confirms the representation of the CP0 critical point with a Lorentz oscillator, i.e., a system with isolated noninteracting levels, the noninteraction also noted from the small value of Γ. The maximum number of electrons per unit cell participating in the transition is 2, the number of electrons in the occupied band. The value of precise 1.0 can be a coincidence and does not necessarily imply a selection mechanism. In particular, surface roughness, which has an rms value of 4 nm for the prepared samples, will reduce the maximum value of the pseudodielectric function profoundly. The actual value of the oscillator strength for $YBa_2Cu_3O_6$ is thus expected to be higher.

The 4-eV transition is attributed to an intraionic transition located in the O(IV)-Cu(I)-O(IV) dumbbell[5–7] and the Cu $3d_{z^2-1}\rightarrow$Cu $4p_x$ transition dominates the dielectric function.[6] At the boundary of the Brillouin zone, these initial and final-state bands were calculated to have a dispersion of

0.5 eV. This results in a strongly peaked emission feature in the calculated dielectric function. However, this emission feature is much broader (0.25 eV) than our experimentally determined Γ, especially considering the strong temperature dependence of this feature and the experimentally extrapolated value of 17 meV. A calculation by Heyen and co-workers[21] mentions that the bands making the dumbbell do not significatly hybridize with the other bands and that the occupied bands just below the Fermi energy can be viewed upon as almost isolated subsystems, i.e., the charge-transfer band and the dumbbell band. The strength of the 4-eV transition and its small width show that this transition originates from a band whose interaction with other bands, and thus its dispersion, is overestimated in electronic structure calculations.

The clear appearance of the broad optical feature at 3.5 eV is surprising, because in existing literature this feature is far more obscure and broadened.[3,7,8] This broadened behavior can be influenced by three reasons. First, in all literature studies, samples are measured *ex situ* in air and formation of (thin) degraded surface layers will influence the measurements as shown above. Second, most studies on oxygen deficient $YBa_2Cu_3O_{7-\delta}$ samples are measured on single crystals.[2,5,7,8] These single crystals consist, in general, of small platelets of twinned crystals, which can also explain the broadening behavior. The apparent lack of temperature dependence indicates that the transition has a nonlocalized nature. The known feature at 2.7 eV is caused by interband transitions between plane Cu-O bands and disappears at higher temperatures in agreement with observations by others.[1,4]

In summary, we have presented *in situ* optical measurements on the temperature dependence of $YBa_2Cu_3O_6$ thin films in the visible-NUV energy region. The results obtained are not influenced by any possible surface degradation upon exposure to atmosphere, a common problem in *ex situ* measurements, which can influence the optical response results. Especially, the amplitude of the $YBa_2Cu_3O_6$ optical transition band at 4 eV is very sensitive to the quality of the sample and is much stronger than previously found in literature. The proposed scaling relation in literature between the amplitude of the 4-eV excitation of the dielectric function of high-T_c superconductors and their oxygen content can therefore only be used between samples of comparable electronic and microstructural properties. The 4-eV optical excitation can be described by a single Lorentz oscillator behavior in the complete temperature range of 20 °C–700 °C. Both, threshold energy and broadening of the peak, are linear with temperature at high temperatures. The measured oscillator strength of the transition is 1.0 electron per unit cell. The large oscillator strength, probaly even damped by surface roughness, combined with the narrow broadening [$\Gamma(T=0$ K)$=17$ meV] indicates that the 4-eV transition is well represented with an optical transition in a two-level system, i.e., an isolated occupied and unoccupied state.

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*Currently at KPN Research Laboratories, P.O. Box 15000, 9700 CD Groningen, The Netherlands.

†Author to whom correspondence should be addressed.

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