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Optical and structural study of BST multilayers

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$Ba_{0.75}Sr_{0.25}TiO_3/SrTiO_3$ multilayers were grown by plasma laser deposition on platinized silicon. Their total thickness was about 300 nm and they consisted of 20 double layers each of thickness 8 nm. X-ray diffraction was used for the characterization of sample microstucture, and surface profiler (alpha step) to determine the film thickness and surface roughness. Optical properties of the multilayers were investigated using spectroscopic ellipsometry and normal-incident reflectivity in the spectral range (1 - 14 eV) at room temperature and their temperature dependence using ellipsometry. The optical parameters of the Pt-coated substrates were fitted using the Drude model and then kept fixed in the subsequent calculation. In the transparent range the spectra were modeled by the Cauchy and Urbach formulas. Direct fit procedure and several models were applied to evaluate optical constants and film thickness. The ellipsometric and reflectivity data were combined to calculate the optical constants and absorption edge.

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1. Introduction

Ferroelectric thin films crystallizing in perovskite structures such as $(BaSr)TiO_3$ are important for a wide range of applications [1]. They are utilized for both their dielectric and optical properties. In informatics, they offer high application potential in DRAM memories, due to their high permittivity. In high-frequency applications they are suitable for the nonlinear variation of their permittivity with the applied electrical field. The large electro-optical coefficient is another attractive property, which prioritizes this material for application in electro-optical devices.

The optical response functions (n and k) and bandgap E_g have been reported by several authors for BST thin films [2-5]. Large variation of the data, especially for E_g (3.2 – 3.8 eV) reported in literature, could be a consequence of different preparation conditions. The precise position of the band gap and its character (direct or indirect) remains still an open question.

In the present study, the $Ba_{0.75}Sr_{0.25}TiO_3/SrTiO_3$ [BST/STO] multilayer structures were prepared and their structural and optical characteristics studied. Special attention was given to the characteristics describing the periodicity of the multilayers. As to our knowledge there are no data for such system.

2. Experimental

The multilayer structures for our study were prepared by pulsed laser ablation, which seems to be prominent among other deposition techniques because it provides high quality thin films that preserve the stoichiometry of multicomponent target. This technique also guarantees high deposition rate, flexibility of deposition conditions and composition control. The BST/STO structures were deposited on 0.5 mm thick platinized silicon, which is a $Pt(111)/TiO_x/SiO_2/Si(100)$ structure. Before the deposition the platinized substrates were carefully cleaned by ultrasound and in vapors of organic solvents. The structures were fabricated from 8 nm thick (approx. 20 unit cells) BST and STO layers, respectively, repeated 20 times. Their nominal total thickness was about 300 nm and was further specified by alpha-step and ellipsometric measurements. The experimental setup and details of the deposition are described elsewhere in detail [6]. A pulsed KrF excimer laser (LUMONICS PM 842 laser, pulse length $\Delta t \sim 20$ ns, repetition rate of 10 Hz) was alternately focused onto a rotating stoichiometric BST or STO targets (diameter of 15 mm, thickness of 6 mm) at an incidence angle of 45° and its energy density flow was 2 Jcm^{-2}. The films were deposited on substrates at temperature varying from 450 to 800°C. All films were prepared in oxygen atmosphere at pressure 0.1 Pa and the target-substrate distance was 70 mm. The base pressure in the deposition chamber was 10^{-3} Pa.

Variable angle spectroscopic ellipsometry (VASE) has been used as a tool for investigation of optical properties of BST thin films. The VASE (J.A. Woollam Co.) spectrometer was working in a rotating analyzer mode in the spectral range 1- 6 eV at incidence angles 65, 70, and 75° at room temperature. Near-normal spectroscopic reflectivity (NNSR) measurements at room temperature were carried out in the spectral range 1 – 6 eV using a Shimadzu UV-1601 spectrometer and a Beaudouin MVR-100 spectrometer for the range 5 – 14 eV.

The structural phase analysis and degree of orientation were investigated by X-ray diffraction at two different geometrical setups using Cu Kα radiation and Seifert XRD7 and Philips X'pert diffractometers.

3. Results and discussion

We concentrated on the sample deposited at 650˚C, which was of the highest quality (sharpest Bragg reflection and no other phases) among the samples prepared at different temperatures. The structure of the multilayer thin films was investigated by X-ray diffraction and reflectivity measurements. In symmetrical wide angle scans all diffraction patterns reveal well separated satellite peaks around the expected basic reflections of the components. Periodicity (or thickness of bilayers) was determined from the position of the satellites of 100 and 111 reflections. The results are summarized in table 1.

The satellite group 100 of the selected sample was studied in detail by calculating and fitting the diffraction pattern by means of the program SUPREX based on a model of real multilayer structure [7]. The resulting fit is shown in Fig. 1 and the refined parameters are summarized in table 1. This fit results in rather unequal thickness of the layers (6.1 and 7.5 nm for BST and STO, respectively). The values of interplanar spacings of constituents are in agreement with the values known from bulk materials. Interface distance between layers was found to be about 0.4 nm, which is roughly the spacing of (100) planes in BST. The total thickness of the multilayer obtained from the diffraction pattern is 272 nm, from X-ray reflectivity measurements the value of 310 nm was found (probably due to a noncrystalline part of the whole structure).

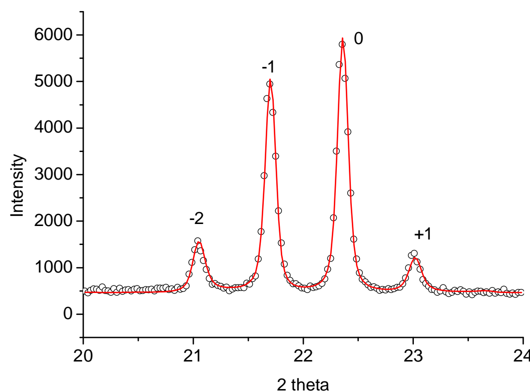

Fig. 1. SUPREX fit of 100 satellite group of the sample deposited at 650 K.

Table 1. Results of fitting for the sample deposited at 650 K (N is number of planes in one stack). Total thickness was 272, 275 and 275 nm measured by x-ray, ellipsometry and profilometry.

	N	Thickness [nm]	Roughness [nm]	Rel. density
STO	19.4(2)	7.5	0.08(1)	0.90(3)
BST	15.0(2)	6.1	0.17(2)	1.12(4)

Spectroscopic ellipsometry deals with the relative changes in polarization of light upon non-normal reflection on the surface of a sample. Its experimental parameters are defined as

$$\rho = \frac{r_p}{r_s} = \tan\Psi \exp(i\Delta)$$

where r_p and r_s are the complex reflection coefficients of the light polarized parallel and perpendicular to the plane of incidence, respectively. The ellipsometric data of the multilayers were taken for three incident angles (65, 70 and 75˚). As an example, the measured Ψ and Δ spectra at the incident angle of 70˚ are shown in figure 2.

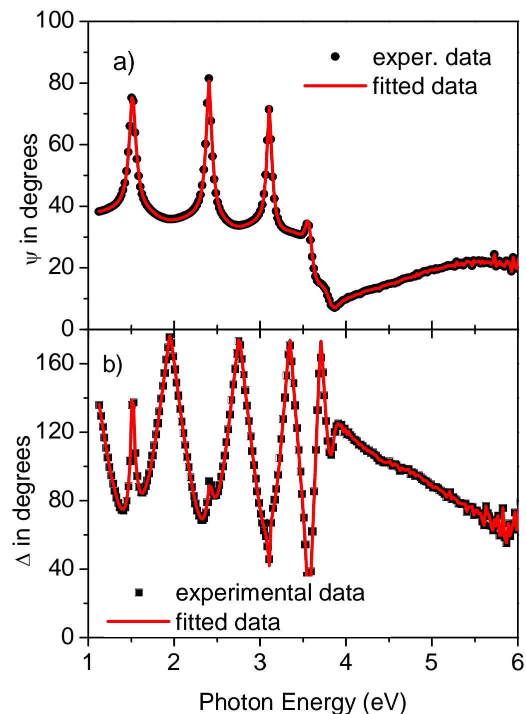

Fig. 2. Frequency dependence of experimental and calculated ellipsometric angles Ψ (a panel) and Δ (b panel) for incidence angle φ=70º at room temperature.

Apparently these spectra and as all others can be divided into two regions: the interference oscillations below the band gap, which originate from multiple reflections within the total thickness of multilayer, and the zone of strong absorption, which originate from the transitions between the valence band and the conduction band. The band gap energy is the point separating the two regions.

The critical point in fitting spectroscopic ellipsometry data is to set a proper structural model with suitable parametrization of the unknown optical response functions. The optical constants of our BST/STO structures derived from the ellipsometric parameters Ψ and Δ were analyzed by a four-phase model consisting of

layers: (air-surface roughness-BST/STO structure-Pt substrate layers). As the Pt layers deposited on substrate were thick enough that the incident light could not penetrate them and they were taken as a semi-infinite medium. Its optical properties were fitted using the Drude-Lorentz model and its parameters were taken constant during further evaluation. In the transparent range below 3 eV, the Cauchy model including the Urbach absorption was used to determine the complex refractive index (*n* and *k*) dispersion and thickness of the BST/STO structure. The ellipsometric thickness, 275 nm with inhomogeneity of 1.6%, was in reasonable agreement with the values obtained by x-ray (table 1, 272 nm) and surface profiler (alpha-step, 275 nm) measurement. The surface layer was modeled as a 50% mixture of averaged multilayer and voids. The dielectric function was calculated by the Bruggeman effective medium approximation. The surface layer thickness was adjusted by refining the fit of the total multilayer structure and the result (3-4 nm) was in good agreement with x-ray and surface profiler data (2-5 nm).

The optical response functions (*n* and *k*) were calculated in the entire spectral interval of ellipsometric measurements. For this purpose the Tauc-Lorentz, Cody-Lorentz, Psemi and point by point procedures [8] were applied. A least squares minimization procedure employing the modified Levenberg-Marquardt algorithm was used to determine their parameters [9,10]. One of the parameters of the first two methods was the optical bandgap E_g.

The optical bandgap was also determined by another method. The frequency dependence of *n* and *k* was specified by using the point by point fitting procedure and then absorption coefficient $\alpha(E)$ was calculated. The optical bandgap energy of the multilayer was deduced from the spectral dependence of the absorption coefficient $\alpha(\nu)$ by applying the Tauc relation $(\alpha(E)n(E)E)^{1/2} = C(E-E_g)$ or Cody plot $(\alpha(E)n(E)/E)^{1/2} = C'(E-E_g)$ [11]. E_g was determined by extrapolating the linear part of the plot and finding the intersection of the line with the *x*-axis. The values of E_g were determined 3.76 and 3.82 eV at 300 and 5 K, respectively, for direct bandgap, and 3.27 and 3.34 eV for indirect bandgap.

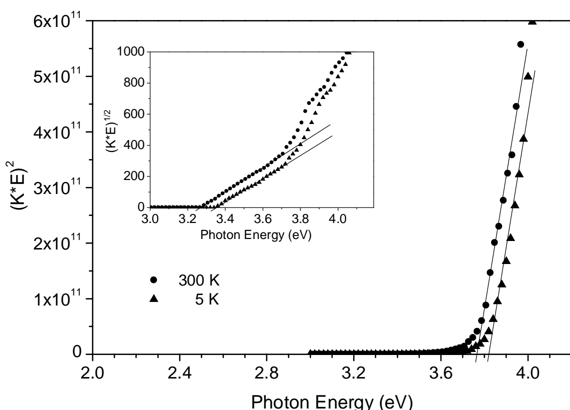

Fig. 3. Tauc's plots for estimation of direct bandgap at two selected temperatures. The inset shows another plot for indirect bandgap.

The optical functions of STO, BTO and BST have been measured several times for either thin films or bulk samples. There is, however, no common agreement about their behavior. This is especially related for the band gap varying from 3.2 to 3.8 eV. There are several reasons for it. Its magnitude depends on the range of absorption coefficients used in the linear fit. According to Zollner [12], there should be direct and indirect band gaps. The first one should lead to a fast increase of absorption coefficient. This is, however, smeared, because the indirect absorption appears below it. The various phonons contributing to it form a tail, which masks the real start of the direct absorption. Some absorption was found below the intrinsic absorption edge (E_g) and was attributed to impurities and lattice imperfections. The detailed mechanism of the absorption is not known at present, but a consequence of the above mentioned effects is a broad knee in the region of absorption edge, which interferes the precise determination of the band gap.

Further extension of the spectral interval from 6 to 14 eV was possible using normal reflectivity measurement. The entire spectrum is a combination of experimental reflectance measured in upper frequency range (6-14 eV) and the reflectivity calculated from VASE measurements (below 6 eV). Good overlap of both spectra was achieved, when the far UV reflectance was corrected taking into account the film surface roughness (~7 nm). Using Kramers-Kronig (K-K) analysis, the phase of the reflected radiation was calculated and subsequently all other optical response functions in the wide spectral range. In this procedure, the calculated phase was corrected by varying the value of the exponent, *l*, in the high-frequency extrapolation term proportional to ω^{-l} in such a way that the phase becomes a smooth continuation of the calculated ellipsometric data. The optimum was found for the value of $l \sim 2.79$. The resulting spectrum of ε_2 is shown in figure 4. There is also its decomposition into elementary Gaussian bands.

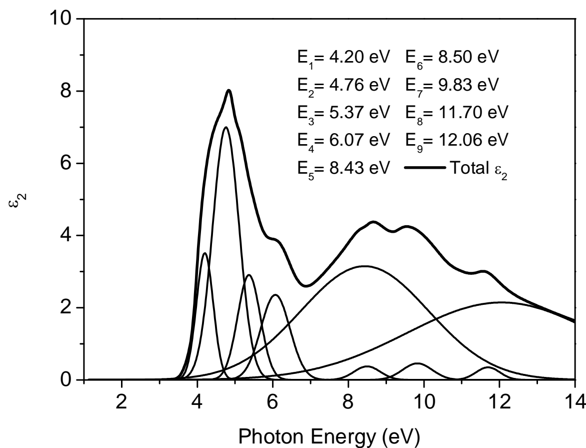

Fig. 4. Decomposition of ε_2 into elementary Gaussian bands. The positions of the band maxima are denoted in this figure.

Temperature dependence of absorption coefficient was determined only by measuring spectroscopic ellipsometry in the temperature range 5 to 300 K. The measurements in cryostat can be carried out only at one incidence angle, which is in our case 70º. We checked that our measurements inside cryostat and outside cryostat at RT were the same. Then we could extract optical response functions for all measured temperatures. The calculated absorption coefficient for two selected temperature is shown in figure 3. Using the Tauc and Cody plots, we determined the bandgap, as is also demonstrated in Fig. 3. Two types of bandgaps (direct and indirect) and their variation with varying temperature were found.

4. Conclusions

BST/STO multilayers with smooth surface and perovskite structure were deposited on platinized Si substrates. XRD, spectroscopic ellipsometry and normal incidence UV reflectance methods were used to characterize their structural and optical properties. The film deposited at 650ºC had the best optical and microstructural properties and was, therefore, selected for further measurement of the temperature dependence of its optical properties. Using several procedures we could determine the magnitude of the direct and indirect bandgap. The most reliable results were obtained, when used the Tauc plot. The temperature dependence of n and k, and E_g smoothly varies and does not indicate any phase transition.

Acknowledgements

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