Optical Properties of Co–$BaTiO_3$/Mg(100) Nano-Composite Films Grown by Pulsed Laser Deposition Method

WU Wei-Dong(吴卫东)[1,2], WANG Feng(王锋)[1,3], GE Fang-Fang(葛芳芳)[1,4], BAI Li(白黎)[1,2], LEI Hai-Le(雷海乐)[1], TANG Yong-Jian(唐永建)[1,2], JU Xin(巨新)[5**], CHEN Zheng-Hao(陈正豪)[1,6], SUN Wei-Guo(孙卫国)[1,3]

[1]*Research Center of Laser Fusion, China Academy of Engineering Physics, PO Box 919-986, Mianyang 621900*
[2]*Department of Physics, Southwest University of Science and Technology, Mianyang 621010*
[3]*Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065*
[4]*Department of Physics, Tongji University, Shanghai 216900*
[5]*Department of Physics, Nanjing University, Nanjing 210093*
[6]*Laboratory of Optical Physics, Institute of Physics, Center for Condensed Matter Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100080*

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Co nanoparticles embedded in a $BaTiO_3$ matrix, namely Co–$BaTiO_3$ nano-composite films are grown on Mg(100) single crystal substrates by the pulsed laser deposition (PLD) method at 650℃. Optical properties of the Co–$BaTiO_3$ nano-composite films are examined by absorption spectra (AS) and photoluminescence (PL) spectra. The results indicate that the concentration of Co nano-particles strongly influences the electron transition of the Co–$BaTiO_3$ nano-composite films. The PL emission band ranging from 1.9 to 2.2 eV is reported. The AS and PL spectra suggest that the band gap is in the range of 3.28–3.7 eV.

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The perovskite-type semiconductors $BaTiO_3$ (BTO) have attracted much attention due to their ferroelectric properties and very strong electron couples. Recent studies have revealed some new phenomena after metal nanoparticles are embedded in BTO matrices. For example, it has been observed by Chen and his co-workers[1−3] that the third-order nonlinear susceptibility $\chi^{(3)}$ and the ratio $(\mathrm{Re})\chi^{(3)}/\mathrm{Im}\chi^{(3)}$ are obviously enhanced when geometric anisotropy nanoparticles are embedded in the BTO matrix. These results are consistent with the theoretical calculations of Sheng *et al.*[4,5] Although up-conversion emission of Er^{3+} doped in the BTO films[6] (the Er^{3+} concentration is about $10^{21}/\mathrm{cm}^3$) has been investigated, the photoluminescence effect of metal-$BaTiO_3$ nano-composite films has not been reported so far.

Table 1. Preparation parameters for growing Co–$BaTiO_3$ films.

Back ground vacuum	$\sim 1\times10^{-5}$Pa
Working vacuum	$\sim 1\times10^{-4}$Pa
Substrate temperature	$\sim$ 650°C at 5 Pa O_2 pressure
Annealing temperature	$\sim$ 650°C
Target	$BaTiO_3$ > 99.9% purity, Co> 99.9% purity
Substrate	MgO(100)
Typical energy density	1.5–2 J/cm^2
Laser pulse frequency	2 Hz for $BaTiO_3$ deposition and 4 Hz for Co deposition

In this Letter, the Co nanoparticles are embedded uniformly in the BTO matrix using a pulsed laser deposition (PLD) technique. The optical absorption (AS) and photoluminescence (PL) spectra are analysed in detail. The preparation parameters are listed in Table 1. Both $BaTiO_3$ and Co targets are mounted on a rotating holder, alternatively ablated by the pulsed laser beam and deposited onto the MgO(100) substrate. The Co concentration in the films is controlled by adjusting the number of laser pulses focused onto the Co target. The characteristics of Co–$BaTiO_3$ films are presented in Table 2. The AS spectra of Co–$BaTiO_3$ nano-composite films were measured by the double beam spectrophotometer for eliminating the influence from the substrate. In the PL spectra, the wavelength for excitation is 250 nm, and the measured range is taken from 300 nm to 750 nm.

Table 2. Characteristics of the Co–$BaTiO_3$ films.

Sample	Thickness (nm)	The number of laser pulse onto the Co target
1	$\sim$ 100	0
1-1	$\sim$ 50	0
2	$\sim$ 100	20
3	$\sim$ 100	40
3-1	$\sim$ 50	40
4	$\sim$ 100	60
5	$\sim$ 100	80
5-1	$\sim$ 50	80
6	$\sim$ 100	120
6-1#	$\sim$ 50	120

The high-resolution transmission electron microscopy (HRTEM), x-ray diffraction (XRD) and Raman spectra show that the single tetragonal-phase Co–$BaTiO_3$ composite films have been prepared by the PLD method.[7] The Co–$BaTiO_3$ composite films

**To whom correspondence should be addressed. Email: jux@nju.edu.cn

are epitaxial with respect to the MgO(100) surface. The c-axis of the films is perpendicular to the MgO(100) surface.[7] Co nanoparticles with anisotropic geometrical profiles taking on polygon are uniformly embedded in the BTO matrix. The absorption coefficient can be calculated according to the equation[8]

$$T(\lambda) = [1 - R(\lambda)]^2 e^{-\alpha(\lambda)d}. \tag{1}$$

For the same material films with different thicknesses d_1 and d_2, we have

$$\alpha(\lambda) = \frac{1}{d_1 - d_2} \ln \frac{T_1(\lambda)}{T_2(\lambda)}, \tag{2}$$

where $T(\lambda)$ denotes the measured transmissivity, and $R(\lambda)$ represents the reflectivity.

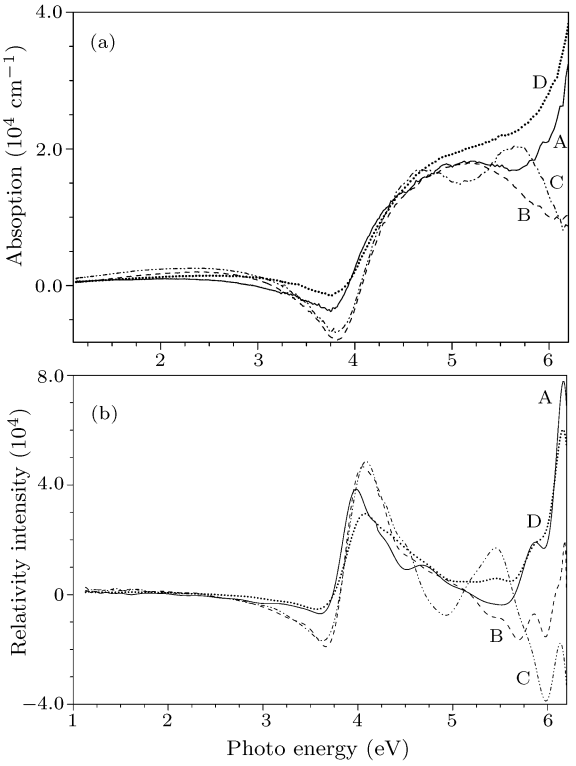

Fig. 1. (a) Absorption spectra: curve A is calculated according to Eq. (2) for sample 1, 1-1 and curves B, C, D for samples 3 and 3-1, 5 and 5-1, 6 and 6-1. (b) The first-order differential spectra: curves A, B, C, D are calculated according to Fig. 1(a).

The absorption and its differential spectra of the Co–$BaTiO_3$ nanocomposite films are shown in Fig. 1. The theoretical calculation[9,10] indicates that the bulk $BaTiO_3$ is of the direct-gap material and the gap of the Γ-point in the first Brillouin zone is about 3.55 eV. Thus the AS around 4.0 eV can be recognized as the absorption edge. According to the equation[11]

$$\alpha \sim \frac{B\lambda}{c}\Big(\frac{\hbar c}{\lambda} - E_{g-opt}\Big)^{1/2}, \tag{3}$$

the optical band gap E_{g-opt} of the Co–$BaTiO_3$ nanocomposite films can be calculated and varies from 4.0 eV to 4.1 eV. The E_{g-opt} estimation of the Co–$BaTiO_3$ nano-composite films is disturbed due to the emergence of the negative absorption nearly at 3.6 eV. These phenomena may result from two reasons, either antireflection for substrate or existence of photoluminescence. Experiments confirm that the existence of photoluminescence is true in this area. If the minimal absorption values are simply reset to be zero, E_{g-opt} of the Co–$BaTiO_3$ nanocomposite films ranges from 3.6 eV to 3.7 eV, in agreement with Refs. [9,10]. Because of the colour centre effect,[11] the wide and weak absorption band in Fig. 1(a) is observed and its centre is determined by the first order differential spectra as shown in Fig. 1(b). The calculation of Fig. 1(b) is described in Refs. [14]. From Fig. 1, the blue-shift of these peaks are obviously observed with the increasing concentration of Co nano-particles and its values are 1.9 eV, 2.3 eV, 2.3 eV and 2.4 eV for curves A–D, respectively.

In Fig. 1(a), the absorption bands in the range 4.0–6.2 eV correspond to the transition from the deeper valence bands to the higher conduction bands of the Co–$BaTiO_3$ nanocomposite films. In this range, the maximum, minimum and saddle point of the absorption curves are the so-called critical points or the Van Hove singularities in the combined density of states.[12] The situations of maximum, minimum and saddle points, i.e. the critical points, can be defined according to the differential spectra shown in Fig. 1(b). The values of middle and extremum points are listed in Table 3.

Table 3. Values of middle and extremum points.

Curve	Saddle (eV)	Maximum (eV)	Minimum (eV)
A	4.72,5.52,5.86,5.97,6.18	5.20	5.65
B	4.05,5.50,5.70,5.84,5.98	5.18	6.08
C	4.08, 5.46, 6.14	4.70,5.64	5.12
D	4.06, 6.18		

From Fig. 1(a) and Table 3, there are five saddle points, one maximum and one minimum in curve A. The theoretical calculation of the energy band structures[9,10] of the pure bulk $BaTiO_3$ indicates that there are several degenerate sub-conduction and sub-valance bands at the point Γ and non-degenerate sub bands at some other high symmetric points such as X points in the first Brillouin zone. Thus the extremum and saddle points are respectively corresponding to the electron transition between sub-bands at the point Γ and other high symmetric points (X point or M point) in the Brillouin zone. In comparison with curve A in Fig. 1(b), the number of saddle points in curve B is invariable and its peak position is dramatically changed because Co nanoparticles are embedded in the BTO matrix. The blue shift of minimum point in curve B states that the combined density of states

at the point Γ in the Brillouin zone is subjected to the influence from Co nanoparticles. For curve C in Fig. 1(b), the absorption band in the high-energy region is split into two absorption bands with the increasing concentration of Co nanoparticles. The two maxima and one minimum are 4.70, 5.64 and 5.12 eV, respectively. In this case, the number and position of degenerate and non-degenerate critical points have all been varied. These phenomena may be illustrated as the presence of some new sub-bands in the conduction and valence band.[13] With the continuously increasing concentration of Co nanoparticles, the AS spectra become unusual in the high-energy region of curve D as shown in Fig. 1(b). In curve D, all the degenerate critical points are disappeared and the number of non-degenerate critical points (saddle points) decreases to two points. Therefore, curve D in Fig. 1(b) displays that the sub-structure of the energy band of Co–$BaTiO_3$ nano-composite films has been greatly changed and this result is in agreement with Ref. [13].

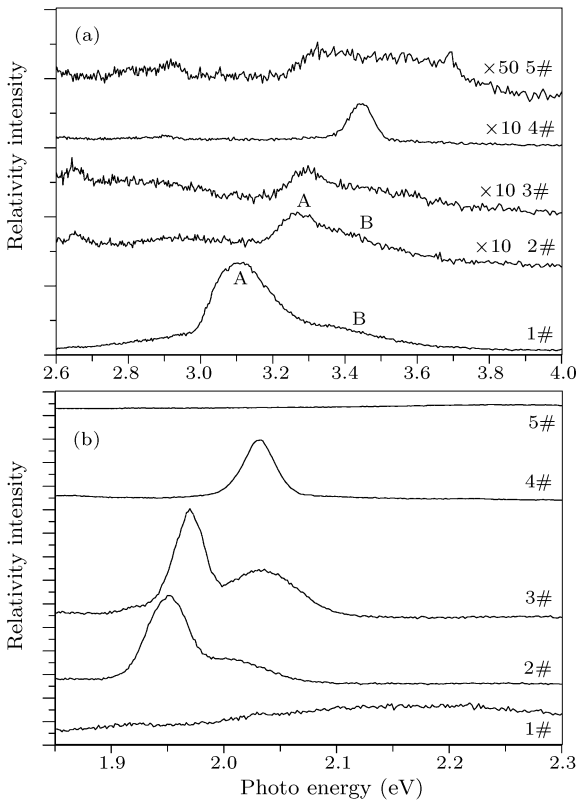

Fig. 2. (a) Photoluminescence spectra in the range 2.6–4.0 eV. (b) Photoluminescence spectra in the range 1.8–2.3 eV.

To further study the effect of Co nanoparticles embedded in the BTO matrix on the optical properties of the films, the room-temperature photoluminescence (PL) spectra are investigated, as shown in Fig. 2. In general, it is difficult to observe the PL emission bands of the pure $BaTiO_3$ crystal. However, two PL emission bands have been detected to range from 2.85 eV to 4.0 eV and from 1.85 eV to 2.1 eV in this work. The two emission bands have never been reported before.

According to the AS spectra and the theoretical calculations,[9,10] the emission bands appeared in the UV range from 2.85 eV to 4.0 eV are the near band gap emission. Indeed, the oxygen vacancies lead to appearance of impurity levels near the bottom of the conduction band.[14−17] Thus, for sample 1, the point A indicates that the electron transition from the impurity levels to the top of the valence band and the shoulder peak point B may originate from the near band-edge emission. In this case, the band-gap E_g is 3.28 eV, which is less than E_{g-opt} while approaches to the calculated value.[9,10] Both of the blue shift and peak weakening have been observed with the increasing concentration of Co nanoparticles, as shown in Fig. 2(a). For the suitable concentration of Co nanoparticles such as sample 4, the impurity level emission is not obvious and the intensity of the band-gap emission increases dramatically. For sample 5, the emission band becomes broader and weaker and its centre shifts to 3.53 eV. It is exhibited that the electron transition from the impurity level and the conduction band to the top of valence band are restrained (or repressed) due to the interaction between the surface plasmon of Co nanoparticles and the BTO matrix.

Figure 2(b) shows the other emission band originating from unknown reason in the visible light region. For pure BTO films (sample 1), there is not any emission in this region. For samples 2, 3 and 4, a strong emission band and blue shift are observed with the increasing concentration of Co nano-particles and their centres are located at 1.95 eV, 1.97 eV and 2.03 eV, respectively. The shoulder peaks are also found for samples 2 and 3 and their values are 2.00 eV and 2.03 eV, respectively. For the higher concentration of Co nanoparticles, all the emission bands are suddenly quenched. These phenomena with the increasing Co nanoparticle concentration, firstly no emission, then strong emission and the blue shift and then suddenly quenching, have never been observed before. These phenomena may originate from the interaction between the surface plasmon of Co nano-particles and the BTO matrix. Although the mechanisms of those emissions have been unclear, this discovery may be applied in tunable semiconductor laser.

In summary, the As and PL spectra exhibit that the optical band gap of Co–$BaTiO_3$ nano-composite films, E_g, is estimated to be in the range of 3.28–3.7 eV. The analysis of the intra-band electron transition of Co–$BaTiO_3$ nano-composite films is consistent with the theoretical prediction. In the high energy range, there are obvious variations in the fine structure of the conduction and valence bands before and

after Co nano-particles are embedded in the BTO matrix. The position, number and topological properties of critical points in the combined density of states apparently in the Co–$BaTiO_3$ nano-composite films have been further studied using the PL spectra and two emission bands have been observed. Specially, the emission band in the range of 1.8–2.2 eV has never been reported before and its centre varies with the concentration of Co nanoparticles embedded in the BTO matrix. This phenomenon may be applied in tunable semiconductor lasers.

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