Write-once medium with BiO_x thin films for blue laser recording

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BiO_x films are prepared by reactive direct current (DC) magnetron sputtering from a metallic bismuth target in $Ar + O_2$ with different O_2/Ar ratios. It is found that the optical property of BiO_x films is sensitive to O_2/Ar ratios and the films deposited at O_2/Ar ratio of 0.5 have the best reflectivity contrast under the same conditions. The structure and optical characteristics of the films are studied by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and spectrophotometer. As revealed by investigations, the phase transition is mainly responsible for the change of optical properties. The static test results indicate that the BiO_x films have good writing sensitivity for blue laser beams. A high reflectivity contrast of about 52% at a writing power of 11 mW and writing pulse width of 800 ns is obtained. In addition, the films demonstrate good stability after being read for 10000 times.

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With the development of high-definition television (HDTV) broadcasting, the capacity of CD or DVD is not enough for high-definition moving pictures to be recorded in high quality. As a result, blue laser recording is proposed and used in optical storage to meet the application requirements for large capacities in a single volume. Among the optical recording systems, the write-once discs become the most popular storage media, due to their low cost and good compliance with read only memory (ROM) discs[1]. Most recording media of write-once optical discs are made of organic materials. However, some disadvantages need to be solved in the blue ray condition, such as optical absorption, thermal stability, and moderate solubility in organic solvents of the organic dye[2]. Therefore, the obvious way to go for write-once media would be an inorganic material sensitive to blue wavelengths. Nowadays, some progress has been made in this field, for instance, Si/Cu[3], Te-O-Pd[4], Bi-Ge nitride[5], and NiO_x[6] have been proposed for blue laser recording. However, the disc structure is still very complicated. So it is significant to explore new inorganic write-once media.

Bismuth oxide is an interesting material due to its optical and electrical properties such as wide band gap, high refractive index and dielectric permittivity, as well as remarkable photosensitivity and photoluminescence[7−9]. Owing to their peculiar characteristics, bismuth oxides are used in various fields, such as gas sensors, optical coatings and microelectronics. Recently, the optical properties of BiO_x films have been studied a lot and it is found that the BiO_x films have a wide band gap of about 3 eV[7,10,11], which is corresponding to the blue wavelength of 405 nm. Furthermore, the optical properties of BiO_x films are strongly influenced by heat treatment owing to the change of structure[12]. Thus, the BiO_x films are supposed to be a good medium for blue laser recording.

In this paper, BiO_x thin films were deposited on K9 glass substrates by reactive direct current (DC) magnetron sputtering using a pure bismuth target in a mixture of argon-oxygen environment with different O_2/Ar ratios. The flow rates of argon and oxygen were individually controlled by flow meters. The base pressure in the deposition chamber was typically 7.0×10^{-4} Pa, while the sputtering pressure and the sputtering power were 0.6 Pa and 150 W, respectively. The simulation of thermal effect of laser on the structure and optical properties of the BiO_x thin films was carried out by a home-made oven. Since the laser-induced temperature on BiO_x films was around 300 °C, the heat-treatment temperature was set at 300 °C. X-ray photoelectron spectroscopy (XPS) (PHI-5000C upgraded by RBD) was used to determine the surface compositions of the films with an X-ray source of Mg Kα (1253.6 eV). In addition, the structures of the as-deposited and annealed films were analyzed by X-ray diffraction (XRD) method (using D/max 2550 V system with Cu Kα radiation). The reflection spectra of the films were measured by a Perkin-Elmer Lambda (900UV/VIS/NIR) spectrophotometer with an accuracy of ±0.01% in the spectral range of 350−700 nm. A home-built static tester with 406.7 nm krypton, mixed-gas ion laser, and objective lens with numerical aperture (NA) of 0.90 was used to evaluate the static recording performance of the BiO_x films. The reflectivity contrast C can be expressed as[13]

$$C = 2|(R_\mathrm{f} - R_\mathrm{i})/(R_\mathrm{f} + R_\mathrm{i})| \times 100\%, \tag{1}$$

where R_i and R_f are the reflectivities of the films before and after writing, respectively. The details of the operating principles of static tester can be found in Ref. [14].

The reflectivity contrasts of the samples deposited at different O_2/Ar ratios are shown in Fig. 1. It can be seen that the reflectivity contrast of the BiO_x films is greatly influenced by the ratio of O_2/Ar and the films prepared at O_2/Ar ratio of 0.5 obtain the best reflectivity contrast under the same condition. Therefore, the films prepared at O_2/Ar ratio of 0.5 were examined in detail. In order to establish the structure, XRD patterns of the films were analyzed by appealing to the International Center for Diffraction Data cards. Figure 2 shows the XRD

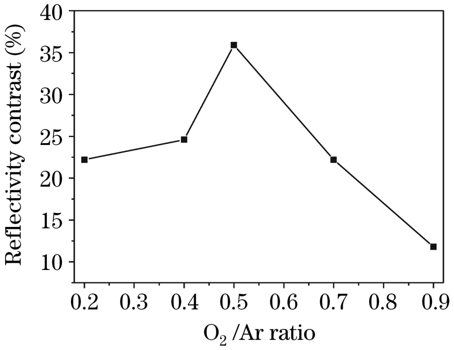

Fig. 1. Reflectivity contrast of BiO_x films deposited at different O_2/Ar ratios under writing power of 9 mW and writing pulse width of 600 ns.

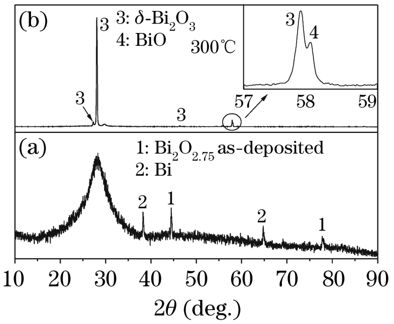

Fig. 2. XRD patterns of BiO_x films deposited at O_2/Ar ratio of 0.5.

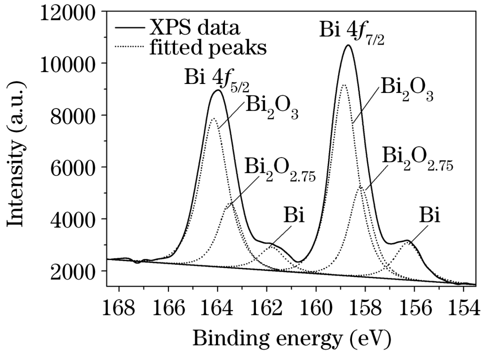

Fig. 3. XPS spectra for $4f$ peaks of Bi of as-deposited BiO_x thin films.

patterns of the samples. The as-deposited films show the presence of mixed phases of tetragonal $Bi_2O_{2.75}$ (card No. 27-0049) and hexagonal Bi (card No. 01-0688), as shown in Fig. 2(a). After annealing at 300 °C for 30 minutes in vacuum, a sharp diffraction peak for face-centered cubic δ-Bi_2O_3 (card No. 27-0052) and hexagonal BiO (card No. 27-0054) is obtained, as shown in Fig. 2(b). Figure 3 depicts the XPS spectra of the $4f_{5/2}$ and $4f_{7/2}$ regions of Bi of as-deposited BiO_x thin films, which were analyzed using appropriate curve-fitting techniques. As shown in Fig. 3, Bi_2O_3, $Bi_2O_{2.75}$ and Bi were obtained in the BiO_x films deposited at O_2/Ar ratio of 0.5. It can be calculated from the XPS peak areas that the molar fractions of Bi_2O_3, $Bi_2O_{2.75}$ and Bi in the as-deposited BiO_x films are 60.7%, 22.0% and 17.3%, respectively. Figure 4 demonstrates the reflection spectra of BiO_x films before and after annealing. It is observed that the reflectivity of the annealed films is always higher than that of the as-deposited thin films in the wavelength range of 350 – 700 nm. It is supposed that the changes of optical properties are related to the phase transition in the process of annealing. Besides, the films exhibit a relatively high reflectance contrast at 405 nm after annealing, which is quite important to blue laser recording.

The static test results of BiO_x films prepared at O_2/Ar ratio of 0.5 are presented in Figs. 5−8. Figure 5 gives the reflectivity contrast of the films as a function of writing laser power. The critical writing power is about 3 mW. And the reflectivity contrast is higher than 35% while the writing power is in the range of 6 – 12 mW. It is quite satisfactory for the requirements of the write-once discs. The reflectivity contrast saturates at about 11 mW, and then gradually decreases. The tendency is similar to the relationship between the reflectivity contrast

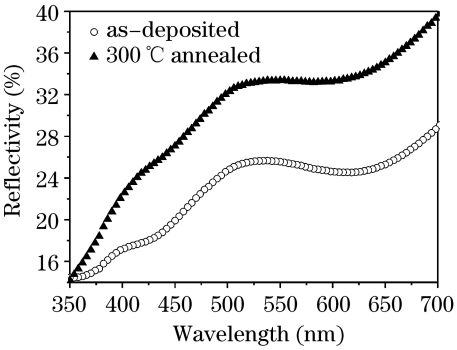

Fig. 4. Reflectance spectra of BiO_x thin films.

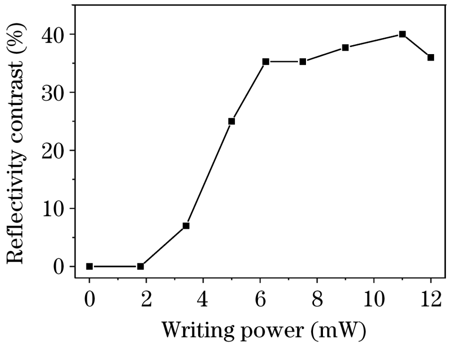

Fig. 5. Dependence of reflectivity contrast on writing power with writing pulse width of 500 ns for BiO_x films deposited at O_2/Ar ratio of 0.5.

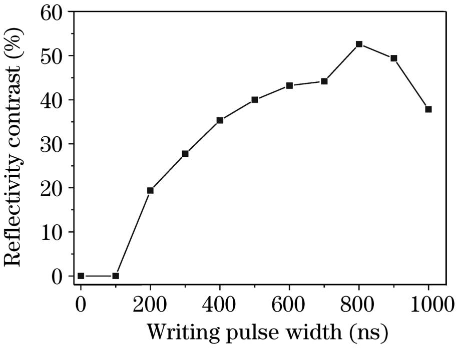

Fig. 6. Dependence of reflectivity contrast on writing pulse width with writing power of 11 mW for BiO_x films deposited at O_2/Ar ratio of 0.5.

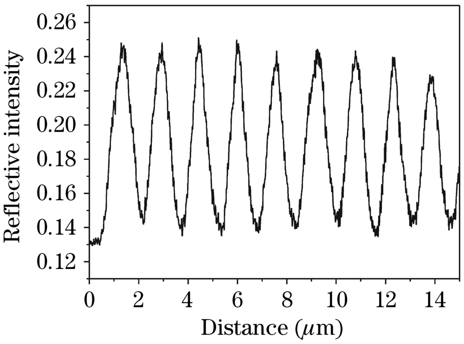

Fig. 7. Reflectivity signals of recording marks for BiO_x films under writing power of 11 mW and writing pulse width of 800 ns.

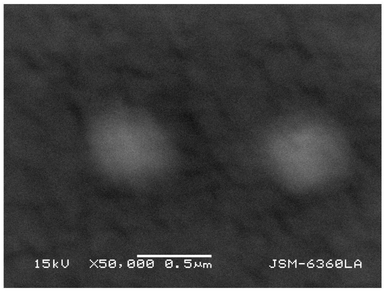

Fig. 8. SEM image of the recording marks.

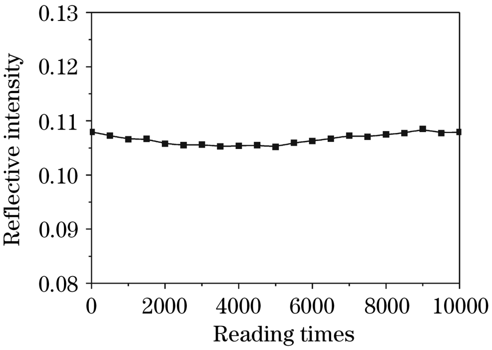

Fig. 9. Dependence of reflectivity intensity versus reading times under reading power of 0.3 mW and reading interval of 10 ms.

and heat-treatment temperature. From the XRD results, it can be supposed that the high reflectivity contrast of the BiO_x films is mainly attributed to the formation of face-centered cubic δ-Bi_2O_3, which is probably the main component of the BiO_x films after laser irradiation. But further studies are needed to confirm whether the formation of hexagonal BiO plays a role in the process. Figure 6 demonstrates the reflectivity contrast of the films versus writing pulse width, which shows an obvious writing pulse width threshold at about 200 ns. When the writing power and writing pulse width are 11 mW and 800 ns respectively, the reflectivity contrast reaches the maximum value of 52%. In order to reduce the writing power and writing pulse width, further research is necessary and should be focused on adding the dielectric layers and optimizing the layer structure. Figure 7 demonstrates the reflectivity signals of recording marks for BiO_x films under writing power of 11 mW and writing pulse width of 800 ns. It shows a good waveform with sharp edges, implying that the BiO_x film is quite suitable for optical recording. Figure 8 is a scanning electron microscope (SEM) image of the recording marks. The diameter of recording marks can reach 450 nm or less while the light spot size D of our optical lens system is 551 nm ($D \sim 1.22\lambda/\mathrm{NA}$). Further studies on reducing the size of recording marks are underway. In addition, the stability of the films is also important for the write-once disc. Figure 9 gives the dependence of reflectivity intensity on reading times under reading power of 0.3 mW and reading interval of 10 ms. It is observed that the reflectivity intensity of the films is nearly stable after reading the same recording mark for 10000 times, which shows the films have good stability.

In conclusion, we demonstrated the possibility of using BiO_x as a recording layer for blue laser beam (406.7 nm). The results of the static test show that the BiO_x films deposited at O_2/Ar ratio of 0.5 possesses the best static recording characteristics with good writing sensitivity and excellent reflectivity contrast. The changes of optical properties may be related to the phase transition of δ-Bi_2O_3 in BiO_x films after annealing, which has a face-centered cubic structure. Further study will be focused on the recording mechanism and film design to optimize the writing power and writing pulse width. The high reflectivity contrast and excellent readout stability demonstrate that the BiO_x films have a high potential to be applied in write-once discs.

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