Short-Wavelength Recording Properties of TeO_x Thin Films *

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We prepare TeO_x thin films by vacuum evaporation of TeO_2 powder. It is found that the as-deposited TeO_x films can represent a two-component system comprising crystalline tellurium particles dispersed in an amorphous TeO_2 matrix. Results of the static recording test show that the TeO_x films have good writing sensitivity for short-wavelength laser beam (514.5 nm). Primary results of the dynamic recording test at 514.5 nm are also reported. The carrier-to-noise ratio of 30 dB is obtained for the disc using a TeO_x film as the recording medium. Atomic force microscopy is used to study the microstructure of recorded marks. Micro-area morphology images show that the marks are mechanically deformed, and depressions and bulges have been imaged in the recorded marks, resulting in the scattering of the reading laser beam. The analytical results of transmission electron microscopy show that there is not obvious difference between the phase states of the tellurium particles before and after laser irradiation. Recording mechanisms of the TeO_x thin films are discussed based on the experimental results.

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In the early 1980s, non-stoichiometric or sub-oxide thin films such as GeO_x, TeO_x and SbO_x with oxygen content lower than the stoichiometric composition were proposed as promising, stable and highly sensitive media for optical disc.[1] Some papers related to these kinds of films were published later.[2−4] Among them, tellurium sub-oxides TeO_x thin films particularly with x between 1.1 and 1.2 were found to be sufficiently sensitive to the diode laser beam and to have excellent stability.[5] The TeO_x thin films showed significant changes in their optical properties such as reflectivity by thermal or optical heating.[6,7] By the addition of Ge, Sn and Pd, the TeO_x thin films have served as a basis for the development of both reversible and irreversible digital optical recording media.[8−11]

It is known that the as-deposited TeO_x thin films represent a two-component system comprising tellurium particles dispersed in an amorphous TeO_2 matrix. However, there are two quite different concepts of the recording mechanism of these kinds of films in the literature. The issues are concerned on the processes occurring in the TeO_x thin films under the action of laser irradiation or heat-treatment since they are based on contradictory data on the structure of the dispersed tellurium particles.

Some researchers reported that the tellurium particles were in an amorphous state in as-deposited TeO_x thin films and the difference of optical properties between the as-deposited TeO_x thin films and the laser-writing marks (or the heated films) was attributed to the segregation of tellurium from TeO_2 matrix and the transformation of tellurium from amorphous to the crystalline state.[5,8,12] However, other researchers [7,11] showed that the dispersed tellurium particles were crystalline even in the as-deposited TeO_x films; after being annealed or irradiated by laser beam, the variations in the optical properties of the films were caused by a significant increase of the tellurium particle size and the migration of tellurium to the upper free surface of the film. All the reported data showed that during the recording process, there was no mechanical deformation of the TeO_x active layer.

In this Letter, based on the experimental results, the recording mechanism of the TeO_x film is discussed and some new explanations are presented.

For most of the studies, single-layer TeO_x thin films were deposited on K9 glass substrates of 30 mm in diameter and 1.2 mm in thickness by a DM220 vacuum evaporation system. TeO_x thin films were prepared by evaporating TeO_2 power (purity, 99.99%) from a molybdenum crucible with 20 V–55 A. During the deposition, the TeO_2 power was just molten, therefore the temperature was near 733°C (the melting point). The different deposition rate could be obtained by adjusting the deposition current. The substrates were ultrasonically cleaned prior to deposition and were neither heated nor cooled intentionally during the deposition. Background pressure of the chamber was less than 3×10^{-3} Pa. The specimens used for the TEM analysis were deposited on carbon-coated copper grids. Thickness of the films was chosen for direct imaging.

The atomic composition and bonding state of the film was measured with a Microlab 310F x-ray photoelectron spectrometer (XPS) equipped with an Mg K_α radiation source. The structure characteristic of the film was investigated by a Hitachi H-800/H-600 transmission electron microscope (TEM) with accelerating voltage 75–175 kV. Thickness of the films was

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measured with an Alpha-Step 500 surface profiler. Surface morphology of the films was examined by an atomic force microscope (Dimension 3100 AFM, Digital Instruments). In order to minimize the interaction with the surface, the tapping mode was preferred to the contact mode. In this mode, a silicon cantilever vibrates near its resonance frequency (193–350 kHz). The tips used were selected with an estimated nominal radius of curvature in the 10–15-nm range.

A home-made static tester was used to evaluate static recording performances of the TeO_x films. In our testers, the argon laser beam with a short-wavelength of 514.5 nm was used. For the static tester, laser pulses of duration from 50 ns to 6 μs with power of 0.1 to 20 mW can be employed for writing and erasing. The laser beam is focused onto the film by a microscope objective with a numerical aperture (NA) of 0.85 to create a spot of about 1 μm in diameter. Reflectivity contrast C can be expressed by

$$C = 2|R_f - R_i/(R_f + R_i) \times 100\%, \qquad (1)$$

where R_i and R_f are the reflectivity of the film before and after writing or erasing, respectively. The details of the operating principles of the static tester may be found in Refs. [13–15].

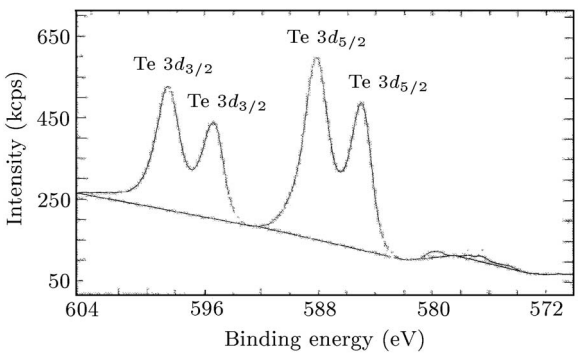


Fig. 1. XPS narrow scan spectra of the Te $3d_{5/2}$ and Te $3d_{3/2}$ region for the as-deposited TeO_x film after etching by Ar^+ for two minutes.

Figure 1 shows the XPS narrow scan spectra on the Te $3d_{5/2}$ and Te $3d_{3/2}$ regions of the as-deposited TeO_x film. Before the XPS measurement, the as-deposited film was sputtered by Ar^+ for two minutes to obtain a clear surface. The peaks of Te $3d_{5/2}$ at 576.6 eV and Te $3d_{3/2}$ at 586.9 eV were assigned to Te^{4+} in TeO_2. The peaks of Te $3d_{5/2}$ at 573.4 eV and Te $3d_{3/2}$ at 583.8 eV were assigned to Te metal. This suggests that the TeO_x thin film composed of Te metal and TeO_2. In addition, the binding energy of O $1s$ was 530.8 eV according to the narrow scan spectra of the O $1s$ region (not shown). The reported binding energies were referenced to the C $1s$ peak region at 285 eV for the sample charging. The atomic percentage (at.%) of Te^0, O^{2-} and Te^{4+} is 24, 25 and 51, respectively, The formula of the as-deposited TeO_x film was about $TeO_{1.04}$. The quantitative analysis was based on the sensitivity factor (SF) and the integral area covered by the typical peak of each element.

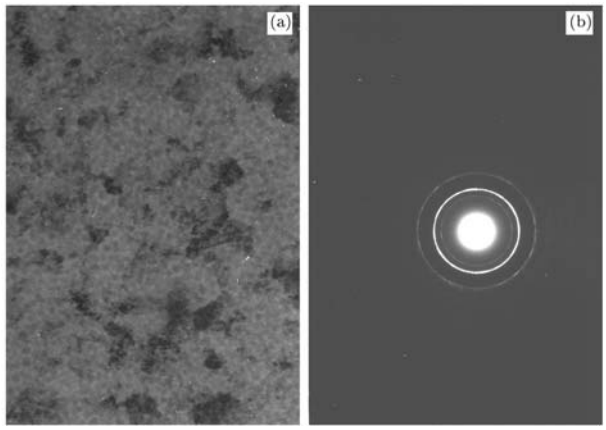


Fig. 2. (a) Bright-field TEM micrograph (50000×) and (b) selected-area electron diffraction pattern of the as-deposited TeO_x film.

Figure 2 shows the bright-field TEM image [Fig. 2(a)] and the selected area diffraction (SAD) pattern [Fig. 2(b)] of the as-deposited TeO_x film. From Fig. 2(a), it could be clearly seen that the as-deposited TeO_x film was built up of a matrix with a fine granular structure and dispersed particles. From the SAD pattern, we could see several diffraction rings with different diameters, indicating the presence of certain poly-crystalline phase. It was confirmed that these diffraction rings were attributed to the dispersed particles. Combining the analytic results of XPS, TEM and x-ray diffraction techniques,[14] it is confirmed that the as-deposited TeO_x thin films can represent a two-component system comprising crystalline tellurium particles dispersed in an amorphous TeO_2 matrix.

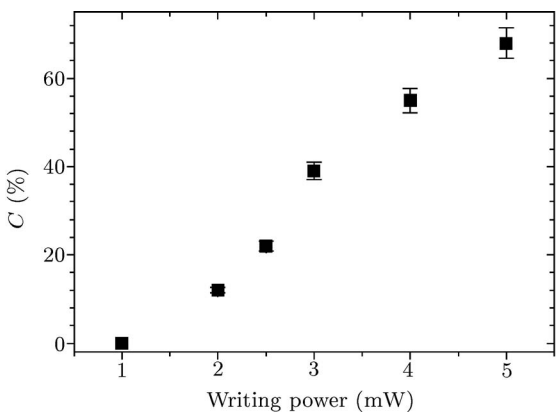


Fig. 3. Dependence of reflectivity contrast C versus writing power with the writing pulse width 100 ns.

Figure 3 shows the reflectivity contrast as a function of writing power with a constant pulse width of 100 ns. The laser beam was radiated from the film-air side. After being recorded, reflectance of the TeO_x thin film decreases. It is obvious that greater contrast can be obtained at higher writing power. It is

also found that at a given power, a larger reflectivity contrast can be obtained in the case of longer pulse duration. If we define that a writing process is fulfilled when C is greater than 15%, the minimum of the writing power corresponding to 100 ns is 2.5 mW. C can amount to 68% at 5 mW. The TeO_x thin film has good writing sensitivity.

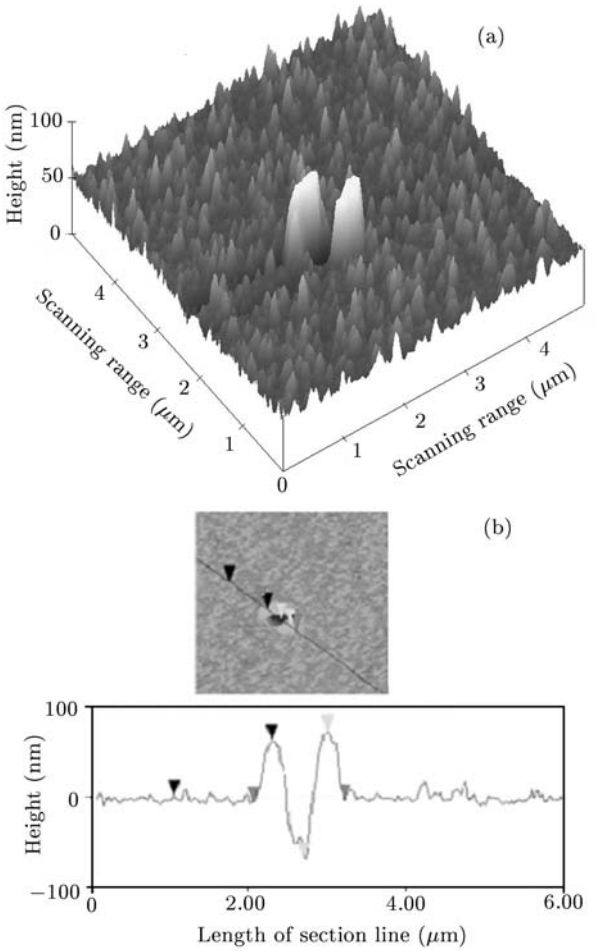


Fig. 4. (a) AFM three-dimensional line scan image and (b) section analysis of the individual mark recorded with the writing power 5 mW, writing pulse width 100 ns. Length of the mark: 1.23 μm, depth of the depression: 77.7 nm, height of the bulge: 60.2 nm.

Figure 4 shows the magnified AFM images of the individual mark recorded with writing power 5 mW, writing pulse width 100 ns. Thickness of the film was about 140 nm. The scan area of Fig. 4(a) is 4.92 μm×4.92 μm. From Fig. 4(a), the micro-area morphology of the recorded mark, which was characterized by a depression in the central region and the bulges on two sides, could be seen clearly. During the writing process, the TeO_x thin film was mechanically deformed and the deformation caused scattering of the reading laser beam. According to the section analysis of the image in Fig. 4(b), the length of the mark is 1.23 μm. The depth of the depression is 77.7 nm and the height of the bulge is 60.2 nm. In the recorded mark, both the bulges and the depressions are not uniform and some little undulations can be found. The fine granular structure of the film also could be seen from Fig. 4 clearly. The as-deposited TeO_x thin films exhibited a rough surface and clusters of the grains appeared in the film. The rough surface and the clusters may be resulted from the non-uniformity produced in the film deposition process. It should be pointed out that, through a specific location method, the AFM can be used to monitor the progress of the surface topography change as a function of the writing power with the constant pulse width of 100 ns.[16] It was found that the level of the deformation was enhanced with the increase of the writing power.

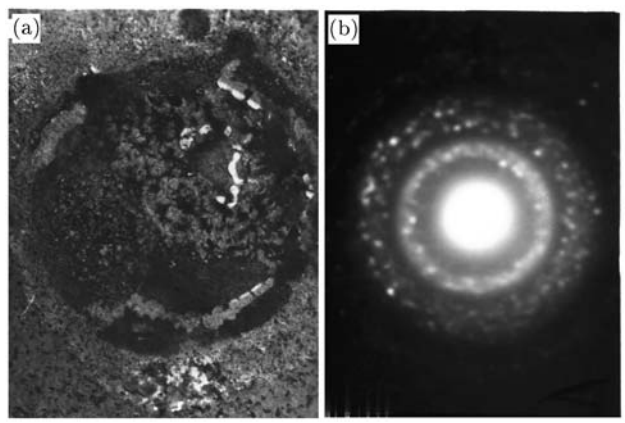


Fig. 5. (a) Bright-field TEM image (10000×) and (b) selected area diffraction pattern of the TeO_x film after being irradiated by a cw argon laser beam with irradiating power 200 mW, irradiating time 30 s.

Figure 5 shows the bright-field TEM image [Fig. 5(a)] and the SAD pattern [Fig. 5(b)] of the TeO_x film after being irradiated by a cw argon laser beam. The power used is 200 mW and the irradiating time is 30 s. The laser beam was focused on the as-deposited TeO_x film by a Fourier lens. The diameter of the irradiated area was about 7 μm. According to Fig. 5(a), there is an obvious difference between the irradiated part and the surrounding area. After being irradiated, the film was ablated and deformed. Segregation of the dispersed tellurium was observed in the irradiated area. The SAD pattern showed the dispersed tellurium particles were still crystalline, there was no obvious diffracting difference between irradiated and surrounding area.

Recordable disc samples using TeO_x films as the media were prepared to evaluate the dynamic characteristics at 514.5 nm. The disc structure was the simple three-layer structure (UV-resin/Al/TeO_x/glass substrate). Both the Al and TeO_x films were deposited by vacuum deposition. To protect the disc, the UV-resin film was deposited by the spin-coating method. The glass substrate is 1.2 mm in thickness and 5.25 inch in diameter. In the experiment, the thickness of the Al films was kept at 100 nm. It is

found that the thickness of the recording layer had much influence on the carrier-to-noise ratio (CNR) of the disc. For 30 kHz bandwidth in the measurement, the CNR $R_{\rm CN}$ can be defined by

$$R_{\rm CN} = \frac{S_{\rm rms}}{N_{\rm rms}}, \qquad (2)$$

where $S_{\rm rms}$ represents the rms signal and $N_{\rm rms}$ denotes the rms noise.

Figure 6 shows the signal curve of the disc with the TeO_x film in thickness 50 nm. The CNR of about 30 dB was obtained with the writing power 10 mW, the writing pulse width 500 ns and the linear velocity about 4 m/s. According to Fig. 6, It could be seen that the low CNR was caused by the relative high level of the background noise which was related to the rough surface of the TeO_x recording layer, the shape of recording bits and tester used.

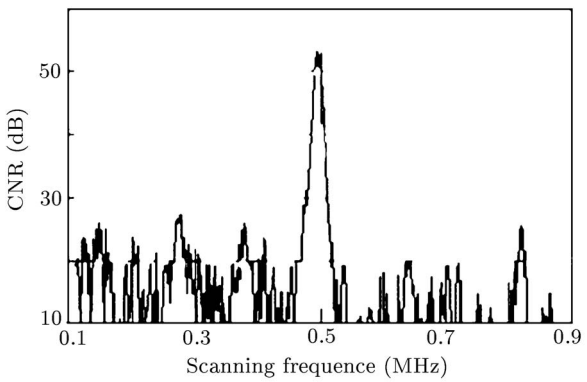


Fig. 6. Signal curve of the dynamic properties tested for the TeO_x film in thickness 50 nm, writing power 10 mW, and writing pulse width 500 ns, at wavelength of 514.5 nm.

Our results of the phase state of tellurium particles in the as-deposited TeO_x films are in contradiction with the concept reported in Refs. [5,8,12]. However, they are in agreement with the other research results of Refs. [7,11]. Since all the concepts are based on the practical experiments, all of them are obviously true. We think the difference is related to the conditions of the films preparation. Based on the reported data, it is difficult to answer this question.

Based on the results mentioned above, some new viewpoints of the recording mechanism of TeO_x films are summarized as below. When the TeO_x thin film is irradiated by a focused writing laser beam, the temperature at the centre of the laser beam is so high that the film is molten and the tellurium grains are segregated and agglomerated.[11,12,14] Further increase of the writing power finally leads to ablation and flow of the film, leading to mechanical deformation in the irradiated area. The deformation is characterized by the bulge and valley in the recorded marks, which causes scattering of the reading laser beam. The level of the deformation is enhanced with the increase of the writing power, so does that of the scatter.[13,16] It is obvious that the reflectivity contrast became higher with the increase of the writing power. In addition, due to the short irradiation time (100 ns), the crystalline tellurium particles may be quenched in the amorphous state when the laser beam is turned off. This is a transient process. However, due to instability of the tellurium amorphous state at room temperature,[17] the amorphous tellurium particles rapidly returned to crystalline state spontaneously. Thus, there is no obvious difference between the SAD pattern of the as-deposited TeO_x film and that of the irradiated area. This mode is different from all the reported ones.

Based on the experimental results and discussion, some ways to improve the recording properties of the TeO_x films could be proposed. First, to decrease the surface roughness of the film and to obtain higher CNR, it is necessary to adopt a new mean such as reactive sputtering to prepare the TeO_x films. Secondly, it is necessary to add properly other new elements to TeO_x films to increase its erasability and melting temperature. In order to obtain higher CNR, it is also necessary to optimize the layer structure.

In conclusion, we have found that the as-deposited TeO_x thin films can present a two-component system comprising crystalline tellurium particles dispersed in an amorphous TeO_2 matrix. The TeO_x films can show a finely granular structure and a rough surface. The results of the static recording test have showed that the TeO_x films have good writing sensitivity for a short-wavelength laser beam (514.5 nm). The CNR of the disc reached 30 dB with the TeO_x film of 50 nm. The AFM observation results showed that the recorded mark is mechanically deformed, leading to the scattering of the reading laser beam. There is no obvious difference between the SAD pattern of the as-deposited TeO_x film and that of the irradiated area. The recording mechanism has been discussed and some ways to improve the recording properties of the film have been proposed.

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