Influence of sputtering parameters on microstructure and mechanical properties of GeSbTe films

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Abstract: $GeSb_2Te_4$ films were deposited on Si substrates by RF magnetron sputtering, and the effects of sputtering power on the surface topography and anti-compression properties were studied with atomic force microscope(AFM) and nanoindenter. Meanwhile, the mechanical properties of $GeSb_2Te_4$ films with oxygen impurity were also investigated. The results indicate that proper sputtering power is important for obtaining $GeSb_2Te_4$ films with high compact structure and low surface roughness, which present good load-support capacity. Although the effect of oxygen impurity on the anti-compression properties of $GeSb_2Te_4$ films is not very significant as a whole, certain oxygen dosage can relax the internal stress, thereby the hardness of the films drops slightly.

Key words: GeSbTe films; sputtering parameters; microstructure; mechanical properties

1 Introduction

Nanometer and atomic scale surface modification on phase-change films using scanning probe microscope(SPM) is a new and promising method to store data with ultra-high density[1−2]. Although the optical and electrical properties of chalcogenide semiconductor have been addressed by many literatures[3−5], its mechanical properties have been rarely reported, especially, the effects of sputtering technical parameters on them have not been addressed so far. Noting that using tip-inducing phase change storage is a contact storage method, it is necessary to investigate the mechanical properties such as anti-compression while studying electric-inducing phase change on the material. Herein, atomic force microscope(AFM) and nanoindenter were employed to characterize surface topography and their mechanical properties of $GeSb_2Te_4$ films deposited with different sputtering powers and oxygen impurity. Thereby, a base is laid to study the phase change storage mechanism of $GeSb_2Te_4$ films and their disc production.

2 Experimental

The $GeSb_2Te_4$ films were deposited on Si(111)

substrates by RF magnetron sputtering equipment, and the compound target with 60 mm in diameter was provided by Mitsubishi Corporation. Two groups of samples were prepared in the experiment. One group alters the sputtering power with other parameters unchanged, and the detailed sputtering parameters are listed in Table 1. The other mainly makes the oxygen input flow vary at the sputtering power of 41 W.

Table 1 Sputtering parameters of $GeSb_2Te_4$ films

Parameter	Value
Sputtering background pressure/mPa	7.0
Sputtering Ar gas pressure/Pa	0.1
RF input power/W	18, 41, 63, 84
Oxygen input flow rate/(mL·min^{-1})	0, 2, 8, 16
Sputtering bias/V	80
Substrate temperature/℃	25
Substrate size/mm	25×25
Target distance/mm	200
Sputtering time/min	40

DI Nanoscope Ⅲ SPM was employed to analyze the surface topography of prepared $GeSb_2Te_4$ films. Nanoindention was conducted with a TriboIndenter system provided by Hysitron Company. The indent tip employed was diamond Cono-Spherical tip, the apex

radius of which is about 2 μm. Nanoindention test result was the average value obtained from four individual tests in different parts of the sample to ensure the reliability. All the tests were conducted on ambient condition.

3 Results and discussion

3.1 Effect of sputtering power

When the sputtering power is not very high, the incident kinetic energy of atoms sputtered onto the substrate is comparatively small due to its own low energy, which leads to low surface transfer rate. Thus the film can easily present three-dimension growth mode, resulting in relatively high surface roughness, as shown in Fig.1(a). With the increment of the power, the roughness deceases, and the amount of island grains increases significantly with the drop of its roughness. In other words, the microstructure of $GeSb_2Te_4$ films becomes stable gradually. It can be seen from Fig.1(c) that at sputtering power of 63 W, the film surface has been quite smooth and compact, and the grains go much smaller. This should be ascribed to the growth transformation from three-dimension mode to two-dimension one, which makes for the optimization of the

structure of the film[6]. Too high power will reduce the surface quality of $GeSb_2Te_4$ films owing to the fact that part of the high energy sputtering particles caused by higher sputtering power collide intensively with the deposited film on the substrate, and the high energy particles play the role of etching the film in some degree accordingly[7−8]. Consequently, this will block the two-dimension growth of $GeSb_2Te_4$ film, and the surface quality of films is much affected, as shown in Fig.1(d).

The hardness and elastic modulus values of the film are mainly obtained by analyzing the load—displacement curves of the loading and unloading process with the nanoindenter[9], thereby the load supporting capacity of tested film can be reflected. Fig.2(a) shows the load—displacement curves of $GeSb_2Te_4$ film deposited by different sputtering powers. Fig.2(b) indicates that the hardness and elastic modulus of $GeSb_2Te_4$ films increase with the increment of sputtering power when other parameters are unchanged. At the same time, considering that the two measured values drop obviously at the power of 84 W, it is believed that there must be an optimum power for the mechanical properties of $GeSb_2Te_4$ film.

Generally speaking, the internal dislocation density
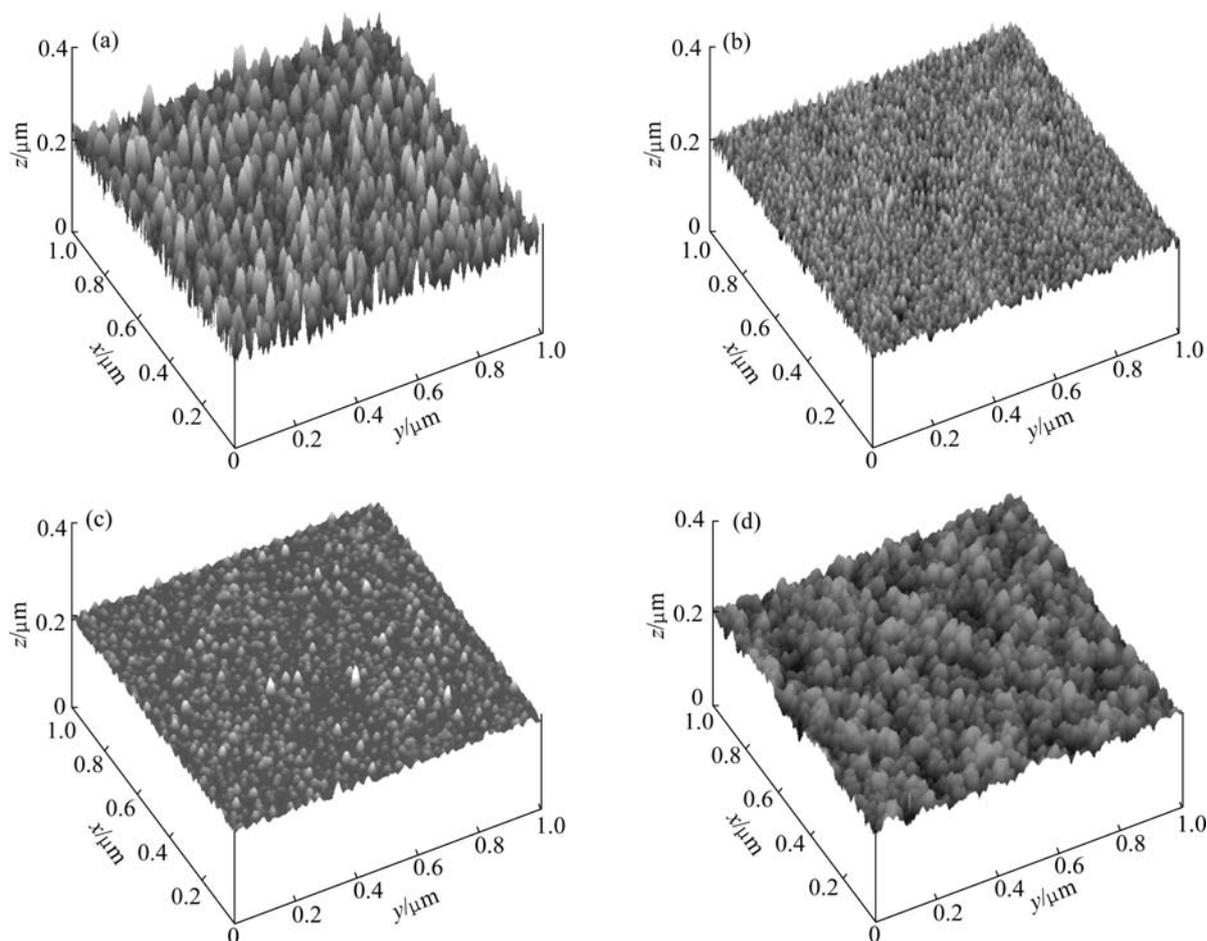
Fig.1 AFM images of $GeSb_2Te_4$ film deposited with different sputtering powers: (a) 18 W; (b) 41W; (c) 63 W; (d) 84 W
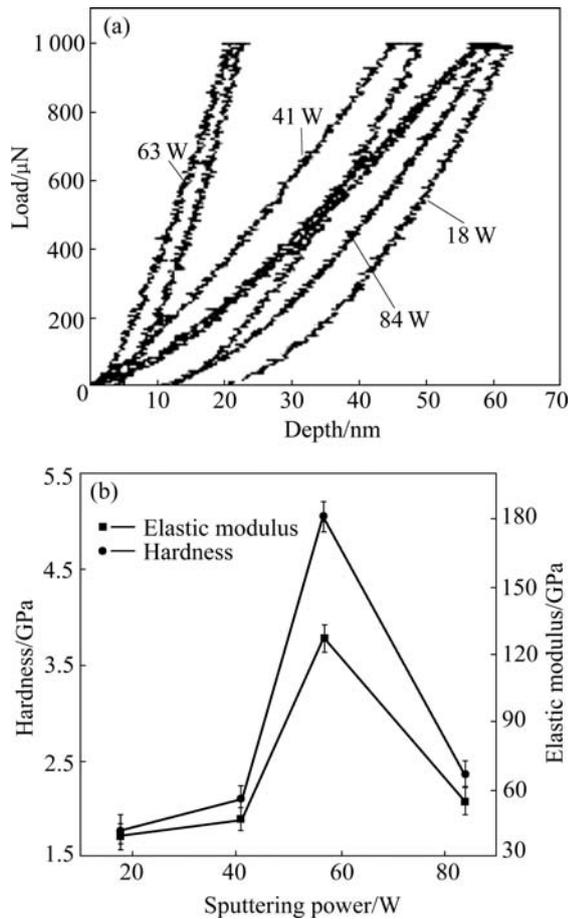
Fig.2 Effect of sputtering power on hardness and elastic modulus of GeSb$_2$Te$_4$ film: (a) Load—depth curves; (b) Variation curves of hardness and elastic modulus with sputtering power

or the structural compaction of the film may be taken into account to analyze the hardness and elastic modulus measured with nanoindenter[10−11]. However, the deposited GeSb$_2$Te$_4$ film by RF magnetron sputtering possesses the amorphous structure. In this case, The mechanical properties of the film should be emphasized particularly on the deformation mechanism of the material under the indenter[12].

Supposing that R_e, R_s and R_d are resistances to compression, shear and compaction or densification for the GeSb$_2$Te$_4$ film underloading of indenter, respectively. The resistance for the deformation, R, would be overlapping of these resistances. Thus their relationship can be written as

$$R \propto (R_e R_s R_d) \tag{1}$$

On this basis, MAKISHIMA and MACKENZIE[13] gave the simplified formulae to calculate the hardness H and elastic modulus E of amorphous glassy material:

$$H = 5.16(\frac{\beta}{10.8\rho_p - 1})^{1/2} \rho_p^{3/2} G \tag{2}$$

$$E = 8.36C \cdot \rho_p \cdot G \tag{3}$$

where ρ_p and G are the packing density of atoms and bonding energy per unit volume, respectively; β is a coefficient directly related to bond strength, and C is a constant.

The above equations mean that the anti-compression properties of the amorphous GeSb$_2$Te$_4$ film greatly depend on the density of its internal packing atoms or the bond strength; in other words, the bigger the packing density or the bonding energy per unit volume of the film, the higher the values of hardness and elastic modulus of the material. So the previous experiment results, combined with the microstructure discussed before, can be considered with the increment of the compaction of the film accordingly. The density of the atoms and the bonding energy increase, so the film has high internal energy density. It is also well accepted that the indent tip must separate the bond between atoms in order to penetrate the material during nanoindention. Thus, the film with higher internal energy density will present certain anti-compression capacity.

YEN[14] also discovered several solid materials whose hardness has a close relation with the density of the atoms and the bond energy. According to the energy density theory, they deemed that classical hardness should be related to the bond density. As to the drop of the hardness and elastic modulus values at the power of 84 W, it may be due to the loose structure caused by too much high energy sputtering particles or oxidation.

3.2 Effect of oxygen impurity

The surface compositions of GeSb$_2$Te$_4$ films deposited with different oxygen flow rates were analyzed by EDX. Evidently, the oxygen content increases in different degree with the increment of the oxygen input flow rate, especially, the content is more distinct at 16 mL/min. Besides, even there is no oxygen input during the process of sputtering, the composition of GeSb$_2$Te$_4$ film, sometimes, still has certain oxygen, due to the degasification of the target clamp caused by the large quantity of heat, which arises from the target and its clamp when the power is comparatively high[15].

Nanoindention results indicate that the effect of oxygen impurity content on the hardness values of GeSb$_2$Te$_4$ films is not as marked as that of the power. The hardness, as a whole, varies between 1.8 and 2.2 GPa, and there is no obvious variation trend (Fig.3). However, the hardness value at certain oxygen content is under the average one. For example, the hardness values at oxygen input flow rate of 2 mL/min and 16 mL/min are lower than that with no oxygen input, about 0.15 GPa and 0.23 GPa, respectively.
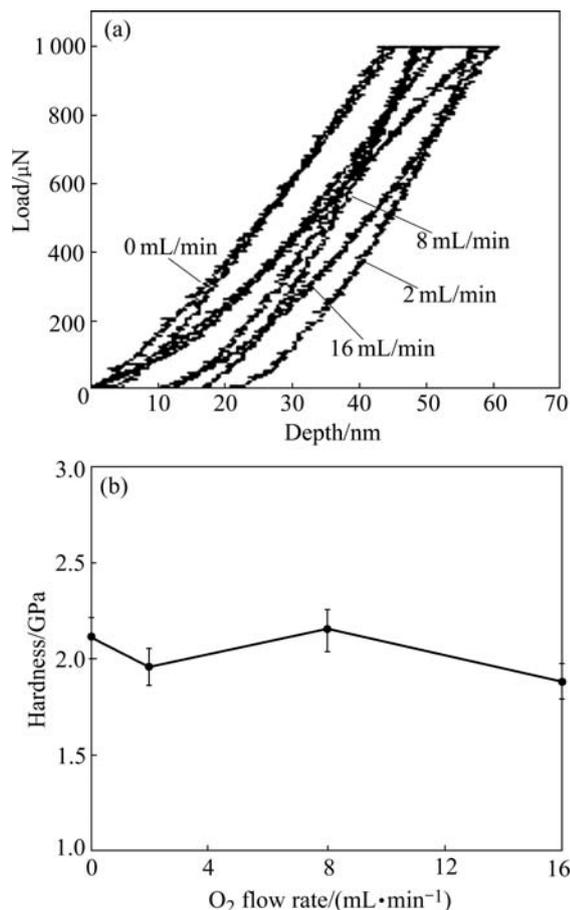
Fig.3 Effect of oxygen amount on hardness of GeSb₂Te₄ films: (a) Load—depth curves; (b) Variation curves of hardness with O₂ flow rate

On one hand, as addressed in Ref.[16], most of the deposited GeSbTe films are in the residual stress state, so part of the oxygen atoms relax the internal stress between Ge-Te, Ge-Sb and Sb-Te structures, thereby the anti-compression capability will decrease to some extent; On the other hand, the oxidation becomes more severe when the extra oxygen is input leading to the looser film structure[17]. In addition, it should be pointed out that the sputtering process is quite unstable when the oxygen is imported into the chamber. Moreover, whether the unstable factor influences the result is still unclear at present, and further research work is under way.

4 Conclusions

1) The compaction of the film goes higher increasingly with the increment of the sputtering power, and the surface roughness becomes smaller due to two-dimension growth mode of the film. Moreover, the anti-compression capacity increases markedly.

2) Too high power is liable to the decrease of the densification of the film, the surface quality and the mechanical properties of the film as well. The energy density theory is adopted to explain the mechanism.

3) The effect of oxygen content on the hardness of GeSb₂Te₄ films is not as significant as that of sputtering power. However, the hardness of the GeSb₂Te₄ films with certain oxygen content drops slightly due to the relaxation of its internal stress.

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