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Mechanical and electrical properties of $GeSb_2Te_4$ film with external voltage applied

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ABSTRACT

A $GeSb_2Te_4$ (GST) film was deposited by RF magnetron sputtering with microwave electron cyclotron resonance plasma chemical vapor deposition equipment. Mechanical and electrical properties together with the morphologies of the film were studied by a nanoindenter which was equipped with nano-electrical contact resistance (nano-ECR) tool and atomic force microscope (AFM). Results show that when no voltage applied between sample and indent tip during indenting, the pile-up phenomenon was observed, the hardness and elastic modulus increases with the load mainly due to the underestimate of the contact area; when external voltages of −7 V, −8 V, −9 V, −10 V were applied, the resistance of the film decreased with applied voltages in about four orders of magnitude, while the elastic modulus increased from 159 GPa to 233 GPa, this changing in mechanical and electrical properties demonstrated that phase change happen during intending, a shrinking region with radius of about 2.5 μm was observed around the indentation when −8 V applied. Furthermore, indent load can also promote the phase change at given negative voltage.

1. Introduction

The use of phase-change chalcogenide alloy films for data storage electrically and optically was first reported in 1968 [1] and in 1972 [2] respectively. Since then, a great variety of promising recording materials have been discovered based on its high speed reversible of amorphous-to-crystalline transformation in thin film materials and utilizes the difference in optical or electrical properties between both states [3–5]. The AFM supplies a method for ultra high density data storage on phase change materials with electrical micro-tips [6,7]. When phase-change happen, the structure of amorphous state which has high resistance changed from face-centred cubic (fcc) to the low resistance hexagonal close-packed (hcp) phase [8–11]. When reading or writing data based on the electrical micro-tips, the tips will slip on the material in contact model, thus the mechanical properties and the surface state of the phase change material may influence its recording properties greatly. Thus is, it is important and necessary to investigate the mechanical, electrical properties and surface structure before and after writing or erasing processes.

Kado and Tohda [12,13] have reported reversible recording in amorphous $GeSb_2Te_4$ films using an AFM with conducting cantilevers, and detect a drop of the electrical resistance of the films when exposed to electrical pulses of −4 V. Ueno and Gan et al. studied the microstructure and morphology of recorded marks in micro area by TEM [14] and X-ray diffraction [15–18], but it is difficult to relocation the recorded marks due to its small size. Ishiyama [19] evaluated the size of phase-change bits by their frictional contrast and deemed it an effective resort for in situ phase-change observation. Jong et al. [20] investigated the load-carrying property of as-deposited GeSbTe media on SiO_2/Si (1 0 0) with the micro-cantilever method and nanoindentation. Ruffell [21,22] used similar instruments which was employed in this paper to study the pressure-induced phase change in silicon during indentation, and in our previous work, the electrical and mechanical properties of nanosilicon, NiCrTiW films and polypyrrole films [23–25] are studied.

In this paper, in situ observations of the micro area morphology together with the mechanical and electrical properties of the GST films are reported.

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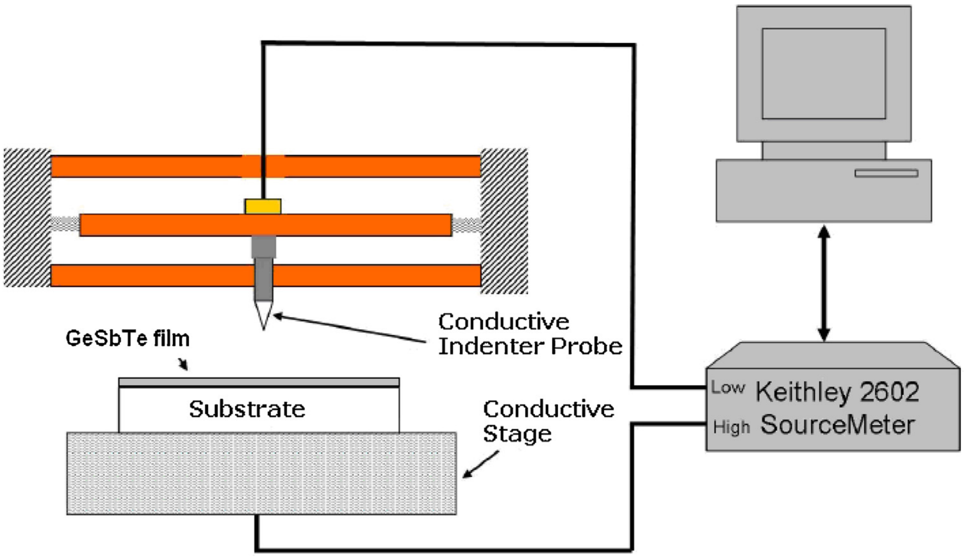

Fig. 1. Schematic diagram of the in situ electrical measurement system in the Hysitron triboindenter.

2. Experiments

2.1. Sample preparation

The GST film was deposited onto Si (1 0 0) by RF magnetron sputtering with microwave electron cyclotron resonance (ECR) plasma chemical vapor deposition equipment. The $GeSb_2Te_4$ target (99.99% in purity) which is commercially available from Mitsubishi Material Corporation in Japan was adopted to deposit the thin film. The detailed deposition parameters of GST film was as follows: the chamber pressure was 5×10^{-3} Pa, the working pressure was 0.1 Pa, the distance between target and substrate was 75 mm, the substrate minus bias voltages were 75 V, respectively, and the deposition time was 40 min.

2.2. Apparatus

An in situ nano tribolab system, which was equipped with nano ECR modulus provided by Hysitron Inc. (Minneapolis, USA) was employed to study the mechanical–electrical properties of thin films. All indentations were performed using the system fitted with a boron-doped Berkovich conducting diamond tip. The nominal resistivity of the tip is 3.3 Ω-cm and the maximum load achievable on this instrument is 10 mN.

Fig. 1 is the schematic diagram of the in situ electrical measurement system. The sample was electrically connected to the stage by a conducting silver paste, then a voltage was applied and the current flow through the sample and tip. An external Keithley 2602 picoammeter/voltage source (Cleveland, OH) was used to provide the voltage potential, to measure the circuit current (sensitivity ∼10 pA) and then transfer it to a personal computer with the Keithley data-logging software. Since the resistivity of the diamond is temperature dependent, all the tests were done at room temperature (23 °C) and a humidity of 25%. Electric current is measured during indentation, and this allows both current monitoring and current–voltage (*I*–*V*) characteristics extraction at various stages of loading–unloading during indenting.

3. Results and discussion

3.1. Mechanical properties

Hardness (*H*) and elastic modulus (*Er*) of the GST film were measured by nanoindentation with different load applied; Results are shown in Table 1, it can be found that both hardness and elastic modulus increasing with load, and hardness varies from 5.2 GPa to 8.7 GPa and elastic modulus varies from 152.5 GPa to 223.0 GPa. Since the thickness of GST film was about 1.5 μm, the effect of substrate can be neglected even for 2500 μN applied, which result in a max depth of only 102 nm, this was far beyond the well known 10% limit [26].

Table 1
Mechanical properties of the GST film.

Load (μN)	*Er* (GPa)	*H* (GPa)
500	152.5	5.2
1000	176.1	5.5
1500	196.9	7.3
2000	209.2	8.0
2500	223.0	8.7

The increasing in mechanical properties at greater penetration depths has two separate origins. Firstly, the size effect, secondly, the effect of pile-up [27], as can be seen in Fig. 2(a). Compare to the mechanical properties of Si, the *H* and E_r of the GST film are smaller, thus the film/subsrate, employeed in this paper is a typical soft film/hard substrate system, then *pile-up* phenomenon of the material inevitably appear during impression, especially for large load. When load of 2500 μN applied, the residual depth was 66 nm, while the height of the pile up was nearly 30 nm (Fig. 2(b)), according to the method provided by O–P [28].

$$H = \frac{P}{A} \tag{1}$$

and

$$E_r = \frac{E}{1-\nu^2} = \frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A}} \tag{2}$$

The contact area *A* in nanoindentation measurements is indirectly deduced from an analysis of unloading data which does not account for pile-up, thus an error in the contact area introduces an error of similar magnitude into the hardness and an error of $A^{1/2}$ in the elastic modulus, which results in overestimations of the hardness and modulus by as much as 60% when we consider elastic modulus and hardness obtained with 500 μN applied as the standard mechanical properties of the film, and this was selected because no evident pile-up is observed.

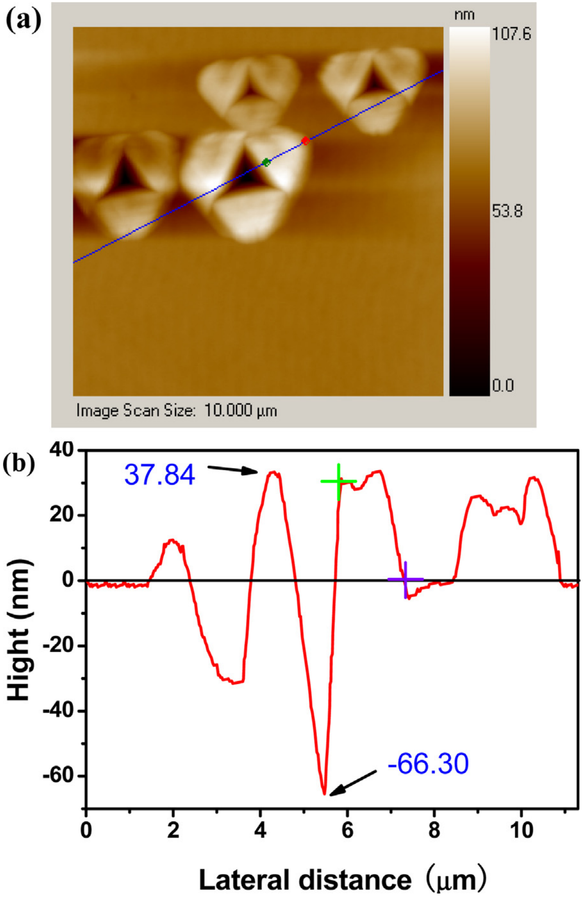

Fig. 2. AFM image and cross section of the GST film, (a) AFM image, (b) cross section of the pile-up.

3.2. Electrical properties

The *I–V* curves of different initial voltages which were extracted by holding the load at maximal load of 500 µN, 800 µN, 1100 µN are shown in Fig. 3 Since the force was a constant value, the contact area between indent tip and sample at max depth should be equal to each other theoretically and the current of each given voltage should also be equal. However, in Fig. 3(a) and (b), almost no current is observed when positive voltage applied to the samples, while for −7 V, −8 V, −9 V, −10 V, an increasing current is observed, especially when the initial voltages was −9 V and −10 V, the maximum current was 0.1 mA, then the current changed almost linearity with the voltage, this means the resistance of the film was constant. Furthermore, the resistance caused by −7 V, −8 V were higher than that caused by −9 V, −10 V. This indicated that the phase change occur for GST film when negative voltages applied. When the voltage increasing to about −1.7 V, all current decreased to 0 A, and this might be caused by barrier between GST grains.

Fig. 3(c) and (d) were the *I–V* curves with indent load of 800 µN and 1100 µN applied separately, and similar electrical properties as that with 500 µN were observed. Contrast to that with −8 V, −9 V, −10 V applied, although the current change of −7 v applied was not prominence, it behaved nonlinearly. This nonlinear changing in current indicated that the phase change still occur even for −7 V, which was higher than that reported by [18]. However, due to the contact resistance among tip/GST, GST/substrate and tip resistance where will also cause the voltage drop, we cannot give simply the conclusion that the threshold value of phase change voltage was −7 V. But as could also be seen in Section 3.3, when the voltages were −5 V and −6 V, no apparent current signal was detected (in the magnitude range of 10^{-7} A) and the mechanical properties change little, this indicated that no phase change happen for these two voltages.

Table 2
Mechanical properties of the film with different voltage applied.

Voltage (V)	Load (µN)	*Er* (GPa)	*H* (GPa)
−5	800	159.3	5.8
−6	800	171.3	5.6
−7	800	230.4	5.2
−8	800	232.9	5.0
+8	800	171.6	5.7

Fig. 4(a) was the three *I–V* curves and the curves of load-indent depth with loads of 500 µN, 800 µN, 1100 µN applied separately, and the sweep voltages increased from −8 V to 2 V. It could be seen that the maximum current at −8 V increased with the load, and in other word, the resistance decreased with the load, furthermore, the decreased rate of the resistance from 500 µN to 800 µN was higher than that from 800 µN to 1100 µN. However, when −9 V and −10 V applied, the maximum current was -1×10^{-4} A for each indent, as was shown in Fig. 3, the indent load affects little on phase change. Thus we may draw the conclusion that indent load can promote the phase change of GST film at low voltage, and the decreasing of resistance at −8 V is the combination of the contact area increasing and phase change.

3.3. Influence of voltage on the mechanical properties

In this section, mechanical properties of the film were tested with voltages of −5 V, −6 V, −7 V, −8 V and +8 V applied at constant load of 800 µN, the curves of load vs. indent depth were plotted in Fig. 5. It can be found that three curves with −5 V, −6 V and +8 V applied were almost superposition, while the curves with −7 V and −8 V applied behaved differently, and the max depth increasing with the decreasing of voltage.

When −7 V and −8 V applied, the indent depth increased quickly at first and then the curves were almost parallel to each other, this could also demonstrated that the phase change occurred at −7 V. The hardness and elastic modulus of the film were given in Table 2. According to Table 2, the hardness decreased with the voltage from 5.8 GPa to 5.0 GPa, while the elastic modulus changed on the contrary, and increased from 171 GPa (−5 V applied) to 232 GPa (−8 V applied). High value of *Er* meant its good deformation resistance, this was mainly because of the material shrinking during phase change from amorphous to the crystalline state [6], and the structure of the film changed from *fcc* to *hcp* the gap.

Curves of the current vs. displacement and load vs. displacement were plotted together in Fig. 6. In Fig. 6(a), the current increased with indent depth when voltage of −8 V applied and at the depth of about 20 nm, the current increased suddenly, this indicated that phase change happened. Similar phenomenon was observed when −7 V applied. However, when −5 V, −6 V applied, the change of current and load curve was correlation (Fig. 6(b)), the current increased with the indent depth without any mutation in current curves, and this was mainly due to the increasing of contact area, and the phase change did not happen.

Furthermore, in Fig. 6, there was sudden decreasing of the current at the maximum depth for each voltage applied, and this exhibited the creep properties of GST film. Fig. 7 gave the load–displacement curve of the indent with 800 µN applied, then the load was hold for 20 s after its reaching to 800 µN, during this period, the depth increased from 40 nm to 54 nm, which demonstrated the existence of creep clearly.

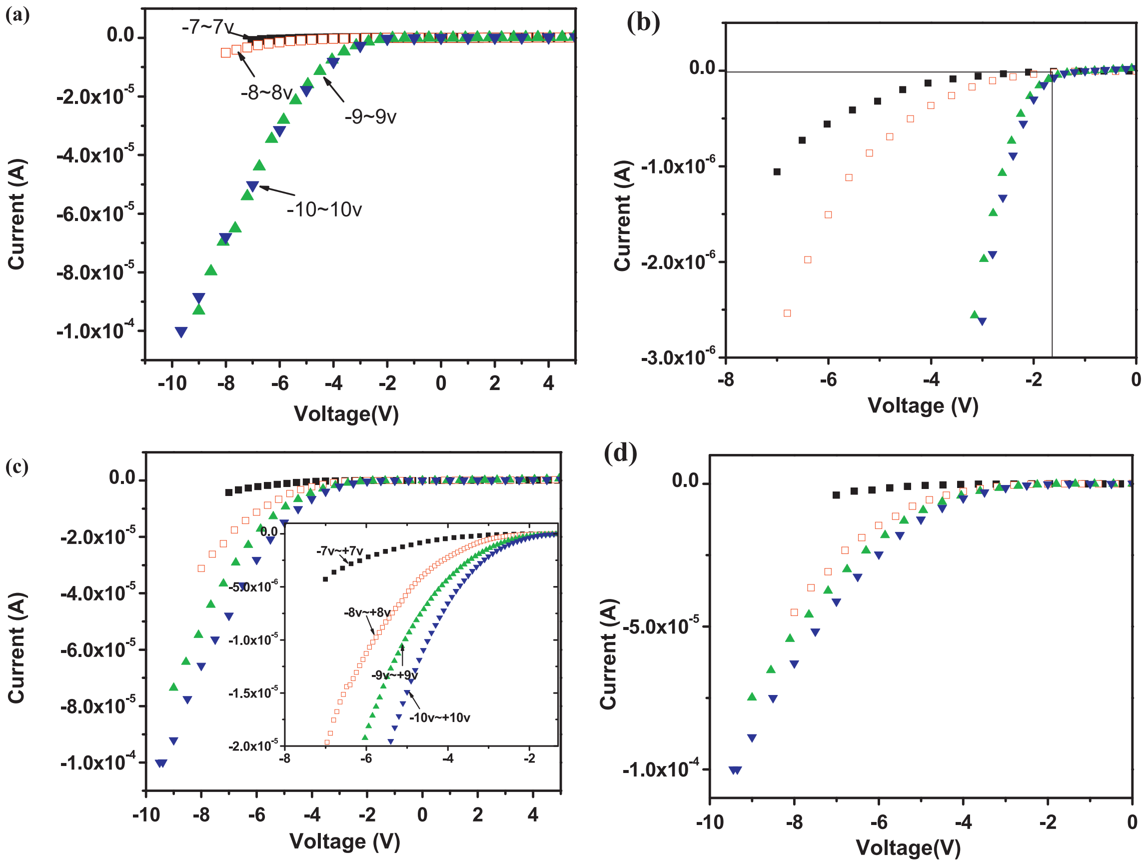

Fig. 3. The *I–V* curves of the sample (a) when the indent load was 500 μN, the *I–V* curves changed with different voltage, (b) enlargement of (a) for negative voltage applied segment, (c) the *I–V* curves of the sample with 800 μN applied, (d) the *I–V* curves of the sample with 1100 μN applied.

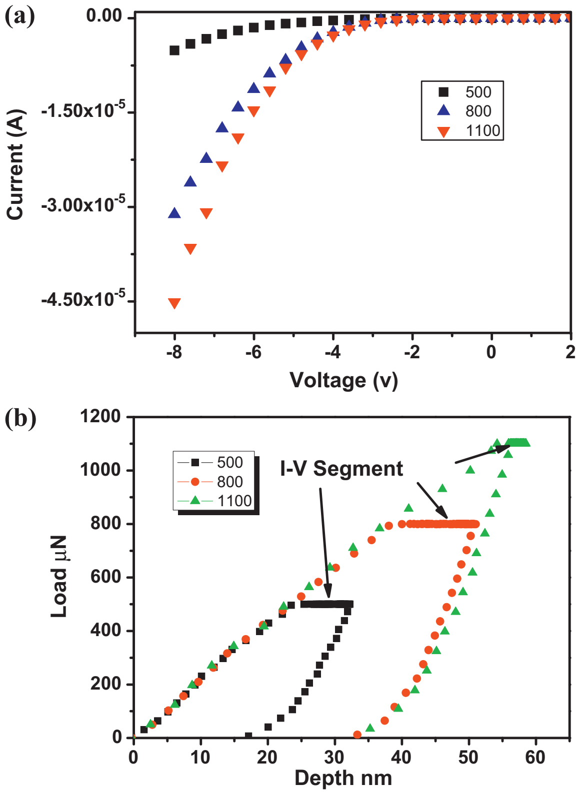

Fig. 4. The *I–V* and load–displacement curves with voltages from −8 to 2 V and 500 μN, 800 μN, 1100 μN applied separately.

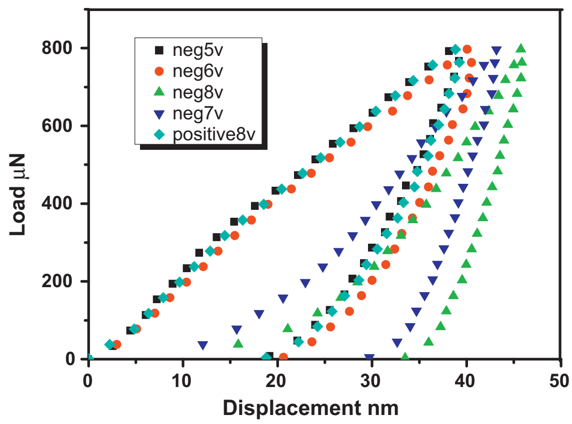

Fig. 5. Curves of load-indent depth with max load of 800 μN and voltages of −5, −6 V, −7 V, −8 V, +8 V.

3.4. Effect of external voltage on the film morphology

Fig. 8 was the AFM morphology of the indentation for GST film. When −8 V applied during indent, there was a circular concave caused by phase change shrinking with radius about 2.5 μm around the indentation, and no pile-up was found, thus accurate hardness and elastic modulus of the film can be obtained by using the method of Oliver and Pharr [26,28]. For comparison, four indents at different positions were carried out with 10 s loading and 10 s unloading with max load of 800 μN, the first one was in the shrinking region (point 1), the second one was at the side of the region (point 2) and the third and fourth one were outside of the region (point 3,

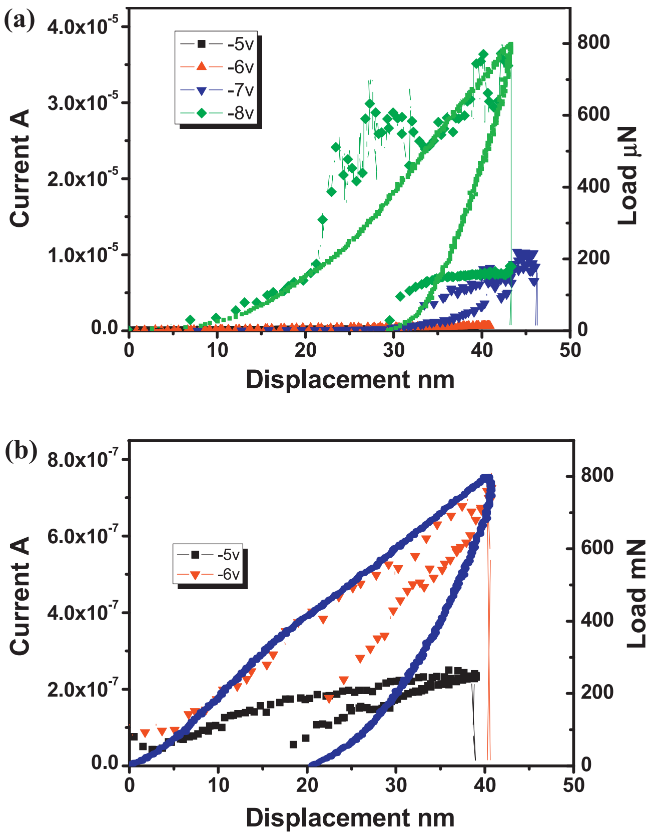

Fig. 6. Curves of current-indent depth with different voltages applied, (a) the current curves with −5 V, −6 V, −7 V, −8 V applied, when the voltages were −7 V and −8 V, there was sudden increasing of the current. (b) The current curves with −5 V and −6 V applied.

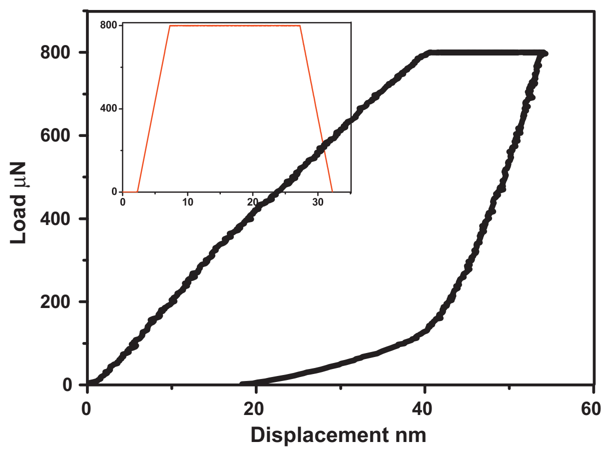

Fig. 7. Load–displacement curve of the indent with 800 µN applied.

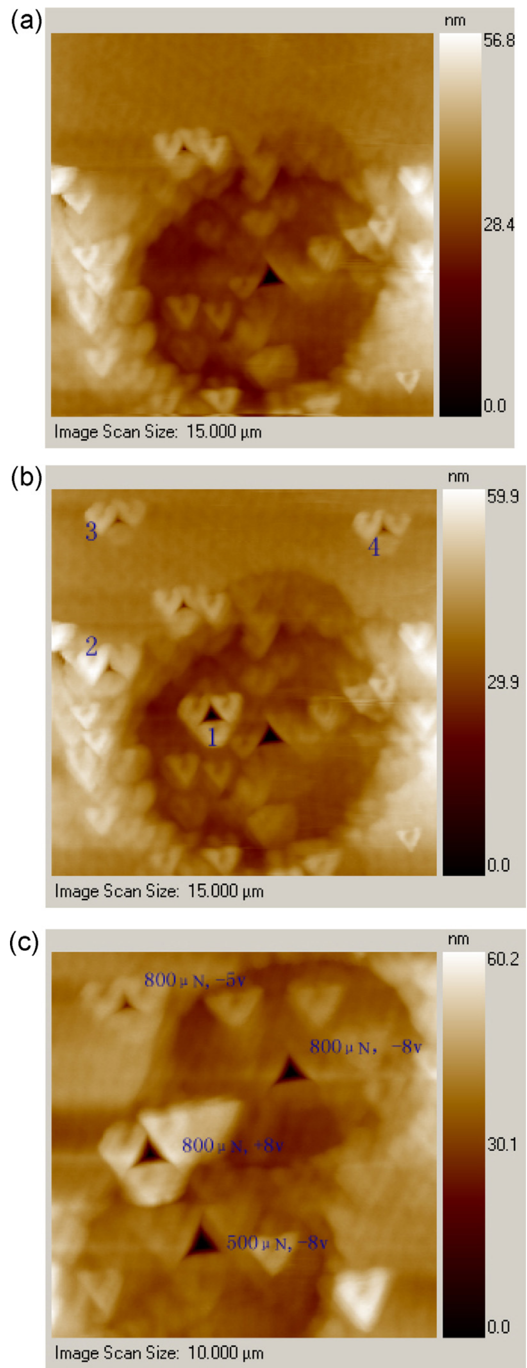

Fig. 8. AFM morphology of the indentations, (a) AFM image of the circular concave phase changed region, (b) AFM image of the four indentations without voltages, (c) AFM image of the indentations with different voltages and loads.

point 4). Hardness and elastic modulus of each indentation were listed in Table 3. It can be found that the hardness of point 1 is only 4.4 GPa and nearly 1 GPa smaller than that of point 2, 3 and 4, however, the elastic modulus of point 1 is 185 GPa, nearly 20 GPa higher than that of point 3, 4, both hardness and elastic modulus of point 1 demonstrated the occurrence of phase change. Hardness and elastic modulus value of point 2 were the smallest except for point 1, because the position was on the transition of phase change and original film, when phase change happen, the structure was loosen and residual force was gathered at this position which would effect the mechanical properties [29].

Table 3
Mechanical properties of the film within and out the phase change region.

Point	Load (µN)	*H* (GPa)	*Er* (GPa)
1	800	4.4	184.1
2	800	5.6	157.4
3	800	5.9	162.6
4	800	5.9	159.9

Fig. 8(c) was the AFM image of the indentations with different voltages and loads applied. It could be found that when −8 V applied during indenting, the circular concave phase-change regions were observed for both load of 500 µN and 800 µN, while for the other two indentations with −5 V, +8 V applied, piles-up instead of circular concaves were observed, but the pile-up of −5 V was smaller than that of +8 V, this indicates that phase change tends to happen when negative voltage applied.

4. Conclusions

A $GeSb_2Te_4$ film on Si was successfully prepared. The mechanical and electrical properties were studied by nanoindenter and its nano-ECR mode. Due to the pile-up phenomenon and the size effect, the measured hardness increases from 5.2 GPa to 8.7 GPa, while the elastic modulus increases from 152.5 GPa to 223.0 GPa, when maximum load increasing from 500 μN to 2500 μN.

The phase change voltage of the GST film is about −7 V, if we ignore the contact resistance. When external voltages of −8 V, −9 V, −10 V applied, the structure changes from amorphous to conducting states, and the resistance of the film decreased sharply. Furthermore, the conducting state of the film owned better deformation resistance property than that of the amorphous state. In addition, indent load could also promote the phase change at given negative voltage. Due to the phase change shrinking of GST film, when negative voltage of −8 V applied during indenting, depression around the residual indentation instead of pile-up phenomenon was observed, and radius of the depression was about 2.5 μm.

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