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Raman spectra and XPS studies of phase changes in $Ge_2Sb_2Te_5$ films*

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$Ge_2Sb_2Te_5$ film was deposited by RF magnetron sputtering on Si (100) substrate. The structure of amorphous and crystalline $Ge_2Sb_2Te_5$ thin films was investigated using XRD, Raman spectra and XPS. XRD measurements revealed the existence of two different crystalline phases, which has a FCC structure and a hexagonal structure, respectively. The broad peak in the Raman spectra of amorphous $Ge_2Sb_2Te_5$ film is due to the amorphous –Te–Te– stretching. As the annealing temperature increases, the broad peak separates into two peaks, which indicates that the heteropolar bond in $GeTe_4$ and the Sb–Sb bond are connected with four Te atoms, and other units such as (TeSb) Sb–Sb (Te_2) and (Sb_2) Sb–Sb (Te_2), where some of the four Te atoms in the above formula are replaced by Sb atoms, remain in crystalline $Ge_2Sb_2Te_5$ thin film. And from the results of Raman spectra and XPS, higher the annealing temperature, more Te atoms bond to Ge atoms and more Sb atoms substitute Te in (Te_2) Sb–Sb (Te_2).

Keywords: $Ge_2Sb_2Te_5$, structure, Raman spectra, XPS
PACC: 7360H, 8130, 7830, 7960

1. Introduction

In 1968, Ovshinsky discovered a new order–disorder memory phenomenon in chalcogenide film materials, later termed 'ovonic memory' and subsequently found a laser optical memory effect.[1,2] Amorphous chalcogenide semiconductor films have been commercially used for the phase-change compact disc rewritable (CD-RW), digital versatile disc rewritable (DVD-RW), digital versatile disc random access memory (DVD-RAM) and blue-ray disc successfully.[3,4] As phase changes occur in these materials, the change in optical constants is accompanied by a much larger change in electrical conductivity. So chalcogenide semiconductor films can also be applied to electrical write and erase nonvolatile memory devices, which is named as ovonic unified memory (OUM).

$Ge_2Sb_2Te_5$ chalcogenide semiconductor has been widely used in rewritable phase-change disc and OUM devices.[5−8] Extensive experimental study using different methods, including AFM,[9] TEM,[10−12] DSC and XRD,[13−17] electrical resistance measurements,[6] ellipsometry investigation,[18] coherent phonon spectroscopy,[19] Raman spectra,[20] numerical simulation,[21,22] has been conducted to understand the crystallization phenomenon and crystalline structure of GeSbTe phase-change material. However, micro-Raman spectroscopy is another powerful tool, which can be used to identify the structure in a small region and to examine molecular clusters. Tominaga and Atoda[20] have reported the Raman spectra of thermally and laser annealed $Ge_2Sb_2Te_5$ films. But the annealing temperature they used was lower than 200°C. X-ray photoelectron spectroscopy (XPS) is very useful for the determination of the binding states of the components. In this paper, we investigate the structure of $Ge_2Sb_2Te_5$ phase change film using micro-Raman spectroscopy and XPS.

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2. Experiments

The $Ge_2Sb_2Te_5$ thin film was deposited by RF sputtering on Si (100) substrate and the temperature of substrate was controlled below 25°C. The substrate was treated as follows: Si (100) substrate was first cleaned in an ultrasonic bath sequentially for 10min each with acetone, H_2O_2+ ammonia solution, H_2O_2+ hydrochloric acid solution, and de-ionized water, and finally was dipped in 4% HF solution to remove the oxide. The background pressure is below 2×10^{-4}Pa. The sputtering parameters of the film are sputtering power of 300W and Ar sputtering pressure of 0.15Pa. The thickness of the film is 200nm, which is determined by Tencor Alpha-Step 500 Profiler. Thin film samples were crystallized by rapid thermal annealing at different temperature under N_2 atmosphere for 1 minute. For the study of Raman spectra (LabRam-1B type Raman spectroscopy), a He–Ne laser (λ=632.8nm) was used as excitation beam and the power density of the laser beam was smaller than 0.1mW/μm^2, which cannot induce crystallization of $Ge_2Sb_2Te_5$. XPS measurements were performed with an XPS spectrometer (Microlab 310F) produced by VG Scientific and the exciting source is Mg Kα.

3. Results and discussions

Figure 1 shows the XRD patterns of the thermal-induced crystallized $Ge_2Sb_2Te_5$ films. Some of the XRD results we have published earlier.[23] It is well known that the as-deposited $Ge_2Sb_2Te_5$ film is in an amorphous state. When the as-deposited $Ge_2Sb_2Te_5$ film was annealed, it began to crystallize from 180°C and the crystallinity increased with the annealing temperature increasing. An analysis of the peak position identifies the crystal structure as the meta-stable face centred cubic (FCC) structure and determines the lattice parameter to be a=0.599nm, which is in good agreement with other report.[24] However, heating the sample to 400°C and 500°C leads to a very different diffraction pattern. The large number of peaks already indicates that the complexity of the unit cell has increased considerably. Yamada *et al*[5] proposed a stable hexagonal structure with a layered structure for this crystalline phase. The size of the hexagonal unit cell was determined to be a=0.422nm and c=1.718nm.[6] These values compare well with our measurements, which determine a=0.4216nm and c=1.7174nm.

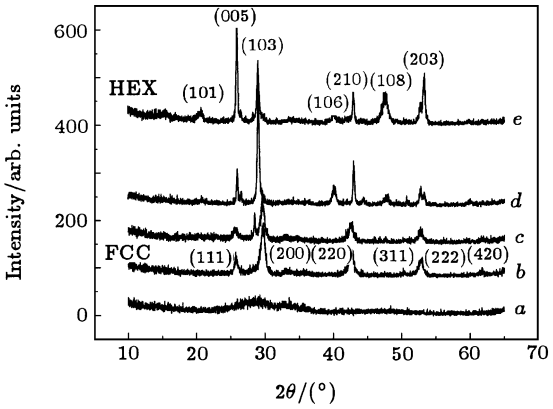


Fig.1. XRD patterns for the as-deposited and thermal-induced crystalline $Ge_2Sb_2Te_5$ films, (a) as-deposited; (b) 250°C; (c) 320°C; (d) 400°C; (e) 500°C. The annealing time is 1min.

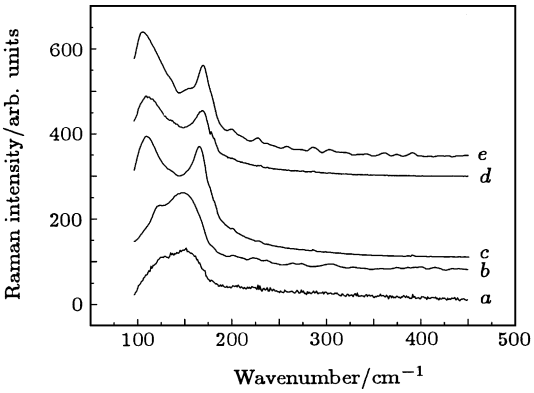


Fig.2. Raman spectra for the as-deposited (a) and thermal-induced crystalline $Ge_2Sb_2Te_5$ films, (b) 180°C; (c) 250°C; (d) 400°C; (e) 500°C. The annealing time is 1min.

Figure 2 shows the Raman spectra of the as-deposited and thermal-induced crystalline $Ge_2Sb_2Te_5$ films at each annealing temperature. From Fig.2(a) we can see that for the as-deposited $Ge_2Sb_2Te_5$ film a broad peak around 151.75cm^{-1} was observed, which may be due to the amorphous –Te–Te– stretching.[20] When the sample was annealed at 180°C for 1min, the broad peak was still at about 150cm^{-1} and began to separate into two peaks [Fig.2(b)]. The two broad peaks can be described as peak A and peak B. Peak A has a lower wavenumber at around 110cm^{-1} and peak B has a higher wavenumber at around 160cm^{-1}. Peak A may correspond to vibration of heteropolar bond in the tetrahedral $GeTe_4$ and/or pyramidal $SbTe_3$.[25–27] Peak B may be due to a Sb–Sb vibration in (Te_2) Sb–Sb (Te_2), in which there is a Sb–Sb bond connected with four Te atoms, and in other units such as (TeSb) Sb–Sb (Te_2) and (Sb_2) Sb–Sb ($SbTe_2$), where some of four Te atoms in the above formula are replaced by Sb

atoms.[28] This assumption results from the fact that this peak does not appear in the film richest in Te and is close to the peak due to Sb bonded to three Sb atoms in the Sb film.[29] The peak A shifts to lower wavenumbers while the peak B shifts to higher wavenumbers as the annealing temperature increases. Due to the phase transition, peak A shifts to 109.84cm^{-1} and peak B shifts to 166.31cm^{-1} at 250°C. And when the annealing temperature reaches 500°C, peak A shifts to 106.98cm^{-1} and peak B shifts to 169.93cm^{-1}.

The Raman shifts may be caused by the structure changes of $Ge_2Sb_2Te_5$ film from the amorphous state to FCC, then to hexagonal structure as the annealing temperature increases, because the atomic arrangements in the above three states are different. The slightly smaller wavenumber in the sample with FCC structure than that with hexagonal structure is ascribed to Sb–Sb bonds in somewhat different environments, where Sb, which is lighter than Te, participates. More Sb atoms substitute Te atoms in (Te_2) Sb–Sb (Te_2), peak B shifts to higher wavenumbers. From the above we can conclude that the crystalline $Ge_2Sb_2Te_5$ film with a hexagonal structure has more Sb–Sb bonds than that with a FCC structure.

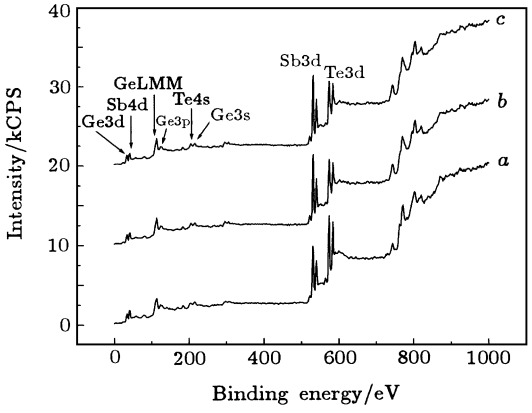


Fig.3. XPS spectra for (a) the as-deposited and thermal-induced crystalline $Ge_2Sb_2Te_5$ film annealed at (b) 250°C and (c) 500°C for 1min.

Consequently, XPS was only used for the determination of the binding states of the components. Figure 3 shows XPS of the as-deposited and thermal-induced crystalline $Ge_2Sb_2Te_5$ films. Due to surface oxidation during the transfer of the films from the deposition device into the analysis chamber, the samples were pre-sputtered for a few minutes to clean the surface of the films. From Fig.3 we can see that when the $Ge_2Sb_2Te_5$ film is in an amorphous state, the bonding energies are 32.6, 531.1 and 573.0 eV for Ge3d, $Sb3d_{5/2}$ and $Te3d_{5/2}$, respectively. For annealing time of 1min, the bonding energy of Ge3d, $Sb3d_{5/2}$ and $Te3d_{5/2}$ shifts to 32.8, 530.9 and 573.1eV respectively for the $Ge_2Sb_2Te_5$ film annealed at 250°C and further shifts to 33.2, 529.3 and 573.1eV respectively for the $Ge_2Sb_2Te_5$ film annealed at 500°C. According to the data in the handbook of x-ray photoelectron spectroscopy, Ge, Sb and Te can be identified in the metallic bond. It is well known that the binding energy of L element, which bonds to M element, increases if M element is replaced by N element and also the electro-negativity of N element is larger than that of M element.[30] The bonding energy of Ge3d increases as the annealing temperature increasing due to more Te atoms bonding to Ge atom because the electronegativity of the Te element is larger than that of Ge element, which is 2.1 and 1.8, respectively.[31] Meanwhile, the bonding energy of $Sb3d_{5/2}$ decreases as the annealing temperature increases due to more Sb atoms substituting Te in (Te_2) Sb–Sb (Te_2) because the electro-negativity of Sb element is smaller than that of Te element, which is 1.9 and 2.1, respectively.[31] Also the bonding energy of $Te3d_{5/2}$ increases slightly due to the electro-negativity of Ge element is slightly larger than that of Sb.[31] The results from XPS are in accordance with those from Raman spectra.

4. Conclusions

$Ge_2Sb_2Te_5$ films were deposited by RF magnetron sputtering on Si (100) substrates. XRD after a heat treatment of the initially amorphous films revealed the existence of two different crystalline modifications of $Ge_2Sb_2Te_5$, which has a FCC structure with lattice parameter of 0.599nm and a hexagonal structure with lattice parameter of a=0.4216nm and c=1.7174 nm, respectively. The broad peak in the Raman spectra of amorphous $Ge_2Sb_2Te_5$ film is due to the amorphous –Te–Te– stretching. As the annealing temperature increases, the broad peak separated into two peaks. Peak A has a lower wavenumber at around 110cm^{-1} and peak B has a higher wavenumber at around 160cm^{-1}. Peak A may correspond to vibration of heteropolar bond in $GeTe_4$ and peak B may be due to Sb–Sb bond connected with four Te atoms, and in other units such as (TeSb) Sb–Sb (Te_2) and (Sb_2) Sb–Sb (Te_2), where some of four Te atoms in the above formula are replaced by Sb atoms, respectively. From the results of Raman spectra and XPS, the higher the annealing temperature, the more Te atoms bond to Ge

atoms and the more Sb atoms substitute Te in (Te_2) Sb–Sb (Te_2) in crystalline $Ge_2Sb_2Te_5$ films. So we can conclude that the crystalline $Ge_2Sb_2Te_5$ film with a hexagonal structure has more Sb–Sb bonds than that with a FCC structure.

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