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Novel material for nonvolatile ovonic unified memory (OUM)–$Ag_{11}In_{12}Te_{26}Sb_{51}$ phase change semiconductor*

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In this paper, $Ag_{11}In_{12}Te_{26}Sb_{51}$ phase change semiconductor films have been prepared by dc sputtering. The crystallization behaviour of amorphous $Ag_{11}In_{12}Te_{26}Sb_{51}$ thin films was investigated by using differential scanning calorimetry and x-ray diffraction. It was found that the crystallization temperature is about 483K and the melting temperature is 754.8K and the activation energy for crystallization, E_a, is 2.07eV. The crystalline $Ag_{11}In_{12}Te_{26}Sb_{51}$ films were obtained using initializer. The initialization conditions have a great effect on the sheet resistance of $Ag_{11}In_{12}Te_{26}Sb_{51}$ films. We found that the effect of the initialization condition on the sheet resistance can be ascribed to the crystallinity of $Ag_{11}In_{12}Te_{26}Sb_{51}$ films. The sheet resistance of the amorphous (R_{amo}) film is found to be larger than $1\times10^6\Omega$ and that of the crystalline (R_{cry}) film lies in the range from about 10^3 to $10^4\Omega$. So we have the ratio $R_{amo}/R_{cry}=10^2 \sim 10^3$, which is sufficiently large for application in memory devices.

Keywords: $Ag_{11}In_{12}Te_{26}Sb_{51}$, phase change, nonvolatile memory, resistance
PACC: 8130H, 7360F

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, digital versatile disc rewritable, digital versatile disc random access memory 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 ovonic unified memory (OUM). This electrical phase change technology has been developed for commercial and space applications by Ovonyx, Inc. at Intel and Lockheed Martin, respectively since 1999.[5] The chalcogenide semiconductor films have two stable states, i.e. the low conductive amorphous state and the high conductive crystalline state, and one state can be converted to the other state by applying electric pulses. OUM is a possible substitute for all kinds of current memory devices such as dynamic random access memory, static random access memory, flash memory, and others. The OUM has a simple cell structure with high scalability; it is nonvolatile which has a relatively high read/write operation speed, and a long cycle life.[6,7] Furthermore, superior radiation tolerance makes it attractive for space-based applications.[8]

Many studies on OUM using chalcogenide semiconductors, such as GeTeAsSi,[1,9] GeTe,[10] GeSbTe,[6,8,11] GeTeBi,[12,13] GeSb (Cu, Ag),[14]

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GeTeAs,[15] In–Te,[16] AsSbTe,[17,18] SeSbTe,[19] and PbGeSb [20] have been reported. $Ag_{11}In_{12}Te_{26}$ Sb_{51} phase-change semiconductor has been used for the rewritable phase-change optical disc.[21] In this paper, we report that it also can be used for OUM.

2. Experiments

The $Ag_{11}In_{12}Te_{26}Sb_{51}$ thin film was deposited by dc sputtering on PC (polycarbonate) substrate, with a background pressure below 5×10^{-4}Pa. The sputtering parameters of the film are: sputtering power 150W, Ar sputtering pressure 1.0Pa. The thickness of the film obtained is 25nm.

The composition of the film was analysed using inductively-coupled-plasma atomic emission-spectrometry (ICP-AES). The structure of the film was examined by x-ray diffraction (XRD) analysis at room temperature using a Rigaku D/MAX 2550V diffractometer. For XRD experiments, Cu Kα (λ=0.15418nm) radiation was used. A differential scanning calorimetry (DSC, Rheometric Scientific DSC-SP type) was employed to measure the crystallization and melting temperatures of the amorphous films at a heating rate of 10, 30, or 50K/min. The film resistance was measured with a four-point probe. We found that the measured sheet resistance R is independent of the sample geometry and can be converted into the resistivity ρ if the sample thickness d is known: $\rho = Rd$. Since the film density changes upon crystallization, the film thickness is not constant during annealing. Therefore, we do not specify the film resistivity, but instead only note the sheet resistance R. To measure the crystallinity dependence of the resistance, the crystallization of the $Ag_{11}In_{12}Te_{26}Sb_{51}$ phase-change thin film was carried out using initializer subjected to various initialization laser powers and velocities. Initialization was performed in a POP120-5F type initializer which was made by Hitachi Computer Peripherals, Japan. The wavelength of the laser was 810nm and the laser beam spot size was $1\times192\mu$m (full width at half maximum). The initialization mode is the constant linear velocity mode. The laser spot feed per rotation (radius) is 96μm.

3. Results and discussion

Figure 1 shows the crystallization and melting temperatures of $Ag_{11}In_{12}Te_{26}Sb_{51}$ phase-change thin film corresponding to the peak of the differential signal from DSC. The crystallization temperatures increase as the heating rate increases. They are 482.3K at 10K/min, 491.1K at 30K/min, and 493.8K at 50K/min. The melting temperature is about 754.8K. Three different crystallization temperatures at different heat rates were used in the Kissinger plot to calculate the activation energy for the crystallization.

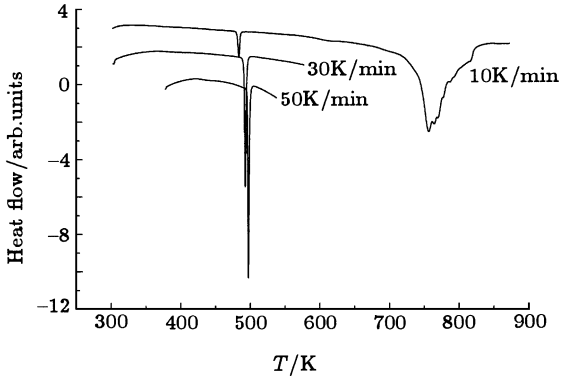


Fig.1. DSC curves for the $Ag_{11}In_{12}Te_{26}Sb_{51}$ thin films at three different heating rates.

For a constant heating rate, v=dT/dt, the Kissinger equation [22] is

$$\ln(v/T^2) = -E_a/(kT) + A, \qquad (1)$$

where v is the heating rate, T is the crystallization temperature, E_a is the activation energy, k is the Boltzmann constant, and A is a constant. A plot of $\ln(v/T^2)$ against $1/T$ yields a straight line (see Fig.2). The activation energy for the crystallization, E_a, was calculated from its slope and turned out to be 2.07eV.

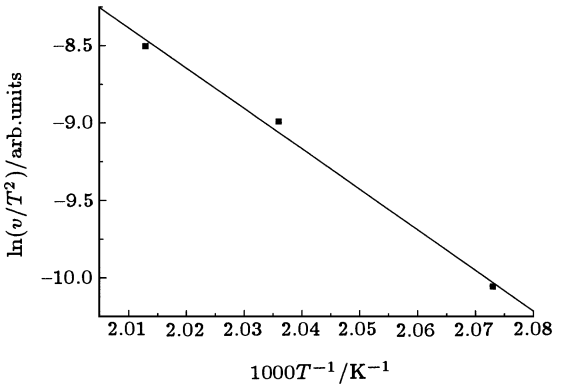


Fig.2. Kissinger plot for $Ag_{11}In_{12}Te_{26}Sb_{51}$ thin film.

Figure 3 shows the XRD pattern of the thermal-induced crystallization $Ag_{11}In_{12}Te_{26}Sb_{51}$ film, which was obtained by subsequent annealing under Ar atmosphere at 623K for 15min. The film thickness is 100nm. It is well known that the as-deposited $Ag_{11}In_{12}Te_{26}Sb_{51}$ film is in an amorphous state. From Fig.3, chalcopyrite $AgInTe_2$, cubic $AgSbTe_2$ and

hexagonal Sb phases were observed in an annealed $Ag_{11}In_{12}Te_{26}Sb_{51}$ film.

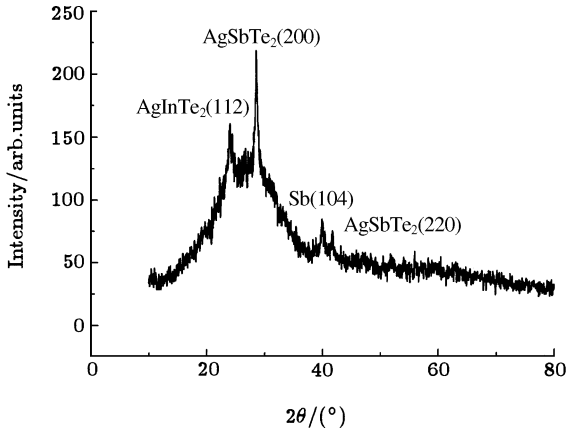


Fig.3. XRD pattern for the crystalline $Ag_{11}In_{12}Te_{26}Sb_{51}$ film.

Figures 4 and 5 show the dependence of the sheet resistance of $Ag_{11}In_{12}Te_{26}Sb_{51}$ films on the initialization laser power and velocity. The sheet resistance of the amorphous $Ag_{11}In_{12}Te_{26}Sb_{51}$ film is larger than $1\times10^6\Omega$. It can be seen that the sheet resistance of the $Ag_{11}In_{12}Te_{26}Sb_{51}$ film first decreases quickly then reaches a steady value as the laser power increases with the initialization velocity (3.6m/s) fixed. With initialization laser power (1300mW) fixed, the sheet resistance increases as the initialization velocity increases. The sheet resistance of the crystalline (R_{cry}) $Ag_{11}In_{12}Te_{26}Sb_{51}$ film changes from about 10^3 to $10^4\Omega$ in our measurement range, $R_{amo}/R_{cry}=10^2\sim10^3$, where R_{amo} is the resistance of the film in amorphous state. The ratio is sufficiently large for application in memory devices.

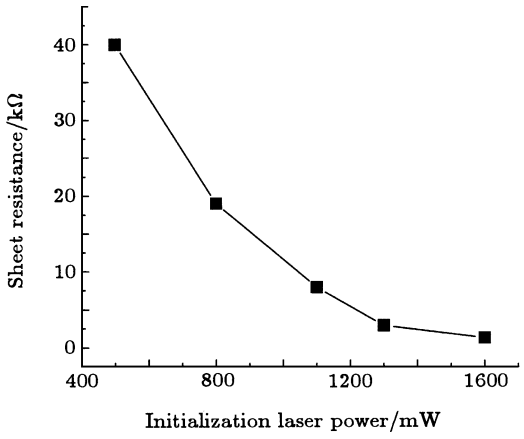


Fig.4. Dependence of the sheet resistance of the $Ag_{11}In_{12}Te_{26}Sb_{51}$ films on the initialization laser power, the initialization velocity being fixed at 3.6m/s.

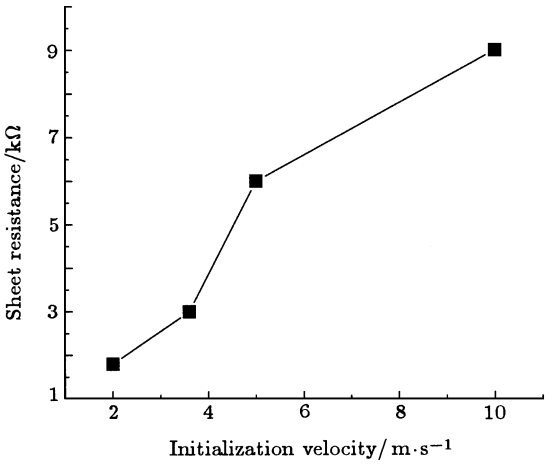


Fig.5. Dependence of the sheet resistance of the $Ag_{11}In_{12}Te_{26}Sb_{51}$ films on the initialization velocity, the initialization laser power being fixed at 1300mW.

The effect of the initialization conditions on the sheet resistance of $Ag_{11}In_{12}Te_{26}Sb_{51}$ films can be ascribed to the crystallinity of $Ag_{11}In_{12}Te_{26}Sb_{51}$ films. For an $Ag_{11}In_{12}Te_{26}Sb_{51}$ film, the higher the crystallinity the lower the resistance, because the amorphous sample is a semiconductor and the crystalline sample is characteristic of metals or semimetals. We have studied the effect of the initialization conditions on the crystallinity of $Ag_{11}In_{12}Te_{26}Sb_{51}$ films.[23] The crystallinity of the film increases with the laser power because the film can be heated to a higher temperature, which is beneficial to crystallization. When the initialization velocity increases, the film is irradiated in a shorter time and the temperature of the film will be lower. So the crystallization becomes difficult and the crystallinity will be lower.

From the above, we can see that the $Ag_{11}In_{12}Te_{26}Sb_{51}$ phase-change semiconductor is suitable to be used in the memory devices. First, the sheet resistance of the amorphous state is very high and that of the crystallization state is low. The ratio of R_{amo} to R_{cry} is large enough for application to the OUM. Second, the melting temperature of the $Ag_{11}In_{12}Te_{26}Sb_{51}$ film is much lower than that of $Ge_2Sb_2Te_5$ film whose melting temperature is about 819K. [24] The $Ge_2Sb_2Te_5$ film is widely used in OUM devices now. This is very useful for reducing the recording voltage and then lowering the energy cost. Third, alloys capable of rapid crystallization have been developed for use in rewritable optical discs.[25] Finally, the resistance of the $Ag_{11}In_{12}Te_{26}Sb_{51}$ film can be changed continuously in a very large range if the crystallinity changes. This phenomenon can be

applied to multilevel recording, which results in high-density memories. The researches on the electrical switching in the memory cells are underway now.

4. Conclusions

The $Ag_{11}In_{12}Te_{26}Sb_{51}$ phase-change semiconductor is suitable to be applied to the OUM device. For the amorphous $Ag_{11}In_{12}Te_{26}Sb_{51}$ thin film, the crystallization temperature is about 483K and the melting temperature is 754.8K, with an activation energy for crystallization, E_a, 2.07eV. As the crystalline $Ag_{11}In_{12}Te_{26}Sb_{51}$ phase is composed of $AgInTe_2$, $AgSbTe_2$ and Sb phases, the crystallinity has great effect on the sheet resistance of the $Ag_{11}In_{12}Te_{26}Sb_{51}$ crystalline film and the sheet resistance of the crystalline (R_{cry}) film changes from about 10^3 to $10^4\Omega$. The sheet resistance of the amorphous (R_{amo}) film is larger than $1\times10^6\Omega$. So the ratio of R_{amo} to R_{cry} is ($R_{amo}/R_{cry}=$) $10^2 \sim 10^3$. This ratio is sufficiently large for application in the memory devices.

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