Crystallization kinetics of Cu/a-Si bilayer recording film under thermal and pulsed laser annealing

Yung-Chiun Her and Chun-Lin Wu
Department of Materials Engineering, National Chung Hsing University, Taichung 40254, Taiwan, Republic of China

(Received 17 February 2004; accepted 8 August 2004)

The crystallization kinetics of Cu/a-Si bilayer recording film under thermal and pulsed laser annealing has been studied. Under thermal annealing, the crystallization temperature and activation energy for crystallization of a-Si with a thin Cu metal layer were reduced to about 485 °C and 3.3±0.1 eV, respectively. The reaction exponent was determined to be around 1.8, corresponding to a crystallization process in which grain growth occurs with nucleation, and the nucleation rate decreases with the progress of the grain growth process. Under pulsed laser annealing, the activation energy for crystallization of a-Si was estimated to be about 0.22 eV which is significantly lower than that under thermal annealing and may be explained by the explosive crystallization of a-Si, while the reaction exponent was found to vary from 1.2 to 1.4, corresponding to a grain-growth-controlled process associated with instantaneous nucleation. © 2004 American Institute of Physics. [DOI: 10.1063/1.1803606]

I. INTRODUCTION

Amorphous Si (a-Si) thin film, demonstrating the advantages of environmental friendliness and simple fabrication process, has been adopted as a recording layer for the write-once blue-ray disk. However, the improvement of recording sensitivity and the reduction of crystallization temperature of a-Si recording film are required to increase the recording speed and lower the recording power. It is well known that metal induced crystallization, using metals such as Al, Ag, Au, Cu, Co, Ni, Pd, and Ti, can dramatically reduce the crystallization temperature and shorten the crystallization time of a-Si. Therefore, a metal/a-Si bilayer is expected to be a promising recording layer for high-speed write-once blue laser recording. Recently, Inoue et al. proposed an inorganic write-once blue-ray disk that used a Cu/a-Si bilayer as the recording film and obtained a jitter value of less than 8% with optimal recording power of 5 mW at data transfer rates ranging from 36 to 144 Mbit/s.

Although the capability of the Cu/a-Si bilayer for high-speed blue laser recording has been demonstrated, the crystallization kinetics of the Cu/a-Si bilayer, which is closely related to the recording sensitivity and the archival stability, under thermal and pulsed laser annealing is still not clear. In this work, we investigate and compare the crystallization kinetics of the Cu/a-Si bilayer recording film under thermal and pulsed laser annealing. The crystallization temperature, activation energy for crystallization, and crystallization mechanism of the Cu/a-Si bilayer recording film are determined and discussed.

II. EXPERIMENTAL PROCEDURE

A 5 nm thick Cu thin film and a 20 nm thick amorphous Si (a-Si) layer were sequentially deposited on Corning 7059 glass, silicon, and pregrooved polycarbonate (PC) substrates by an ion beam assisted deposition system. The pregrooved PC samples were then bonded with dummy PC substrates for the static tests. The crystallization kinetics of the as-deposited Cu/a-Si bilayer under nonisothermal, isothermal, and pulsed laser annealing were analyzed quantitatively by monitoring the reflectivity variation with temperature or time during the annealing process. Both nonisothermal and isothermal annealing were conducted by a reflectivity-temperature-time measuring system, where samples were mounted on a Linkam THMS 600 heating stage in an argon protective atmosphere. For nonisothermal annealing, the sample temperature was raised at heating rates of 5, 50, and 100 °C/min, and the reflectivity variation with temperature was monitored in real time. For isothermal annealing, the samples were heated at temperatures of 5, 10, and 15 °C below the crystallization temperature, which was determined by the result from nonisothermal annealing at a heating rate of 100 °C/min, and the reflectivity variation with time was recorded. For pulsed laser annealing, the static test was carried out by a two-laser static tester from Tueoptics, which monitored the reflectivity variation of the Cu/a-Si bilayer recording film with time during the heating and cooling periods of the recording process. Laser 1 with wavelength (λ) of 399 nm was used in pulsed mode for recording, while laser 2 with wavelength of 422 nm was used in cw mode for monitoring the reflectivity variations. Since the static tester employed an objective lens with a numerical aperture (NA) of 0.6, the beam sizes (d), which is often defined as the half-intensity diameter of the airy pattern such that d =0.61λ/NA, of the laser 1 and laser 2 are estimated to be 406 and 429 nm, respectively. The recording powers of laser 1 were chosen to be 6, 8, and 10 mW, and the pulse duration varied from 20 to 100 ns. The crystalline structures of the Cu/a-Si bilayer recording film, after thermal annealing at various temperatures and irradiation by pulsed laser with
various powers, were characterized by transmission electron microscopy (TEM) to identify the crystallization mechanisms of the Cu/a-Si bilayer recording film under thermal and pulsed laser annealing.

III. RESULTS AND DISCUSSION

Figure 1 shows the reflectivity variations with temperature for the as-deposited Cu/a-Si bilayer recording films at heating rates of 5, 50, and 100 °C/min. All the curves were found to exhibit a two-stage reflectivity change as the temperature was increased from room temperature to 600 °C. The first reflectivity change with a slow increase in reflectivity was observed to take place in the temperature range between 100 and 250 °C, while the second one with a steep rise of reflectivity was in the vicinity of 475 °C. To identify the structural changes occurring at each stage, Cu/a-Si bilayer recording films before and after annealing at 300 and 500 °C for 3 min were examined by TEM, as shown in Figs. 2(a)–2(c). In the as-deposited state, the presence of amorphous Si and polycrystalline Cu was observed by the bright-field image and diffraction patterns. After annealing at 300 °C, different grains with sizes less than 10 nm in diameter were distinguished, and new diffraction rings corresponding to a Cu₃Si phase were observed, however, Si still remained in an amorphous phase. As the annealing temperature was increased to 500 °C, in addition to the grain growth of the existing Cu₃Si phase, amorphous Si was found to be fully crystallized to crystalline Si with a (111) preferential orientation. Apparently, as a Cu/a-Si bilayer recording film was heated, the Cu₃Si phase would precipitate first in the temperature range between 100 and 250 °C, leading to a slow increase in reflectivity. This is followed by the crystallization of amorphous Si to crystalline Si (c-Si) at temperature of about 485 °C, resulting in a steep rise of the reflectivity. Normally, the crystallization of a-Si was observed to take place at about 700 °C. It is evident that inserting a thin Cu metal layer could significantly reduce the crystallization temperature of a-Si. These results are consistent with those reported by Russell et al. based upon the sheet resistance.
change with temperature. Figure 1 also shows that as the heating rate was increased, the occurrence of reflectivity changes shifted to higher temperatures. The formation temperature of the Cu$_3$ Si phase, defined as the temperature at the midpoint of reflectivity change, was found to increase from about 162 °C to 175 °C and 180 °C, as the heating rates were increased from 5 °C/min to 50 °C/min and 100 °C/min, respectively. Meanwhile, the crystallization temperatures of a-Si were found to be 455, 485, and 495 °C as samples were heated at heating rates of 5, 50, and 100 °C/min, respectively. These temperature shifts with increasing heating rate can be related to the activation energies for Cu$_3$ Si phase formation and crystallization of a-Si using Kissinger’s equation:

\[
\ln \left( \frac{\alpha}{T_x^2} \right) = \frac{C - \ln E_a}{RT_x} - \frac{t_0}{m}.
\]

Here, \(\alpha\) is the heating rate, \(T_x\) is the absolute phase formation or crystallization temperature, \(C\) is a constant, \(R\) is the Boltzmann constant, and \(E_a\) is the activation energy for phase formation or crystallization. Figure 3 shows plots of \(\ln(\alpha/T_x^2)\) vs \((1/T_x)\) for the as-deposited Cu/a-Si bilayer recording film. From the slopes of Kissinger’s plots, the activation energies for Cu$_3$ Si phase formation and crystallization of a-Si were determined to be 2.8±0.1 and 3.3±0.1 eV, respectively. The activation energy for Cu$_3$ Si formation is similar to that for CrSi$_2$ formation, which was reported to be 2.7±0.3 eV. However, it is higher than that for Ni$_3$ Si formation, which was reported to be 1.5 eV. Meanwhile, the activation energy for crystallization of a-Si with a thin Cu underlayer is about 0.9 eV lower than that for a pure sputtered a-Si, which was reported to be 4.2 eV, indicating that inserting a thin Cu metal layer could also reduce the activation energy for crystallization of a-Si.

In addition to nonisothermal crystallization behavior, isothermal crystallization behavior of the Cu/a-Si bilayer recording film was also investigated. Figure 4(a) shows the reflectivity as a function of time for Cu/a-Si bilayer recording film isothermally annealed at temperatures of 480, 485, and 490 °C. Typical S-shaped transformation curves that composed of an initial slow increase regime, an acceleration regime, and a saturation regime were found. Normalizing the reflectivity change by the total reflectivity difference before and after crystallization, the fraction of crystallization at a given time can be determined. The isothermal crystallization characteristic in the acceleration regime can be described by the Johnson-Mehl-Avrami (JMA) equation. In the JMA equation, the fraction of crystallization \(X\) as a function of time \(t\) is given by

\[
X(t) = 1 - \exp[-K(t-t_0)^m].
\]

Here, \(t_0\) is the incubation time, \(m\) is the reaction exponent, and \(K\) is the rate constant. Figure 4(b) shows the ln[-ln(1-X)] versus ln\((t-t_0)\) plots for Cu/a-Si recording films isothermally annealed at 480, 485, and 490 °C. It was found that the reaction exponent \(m\) for the Cu/a-Si bilayer recording film was independent of annealing temperature, and was determined to be around 1.8, corresponding to a crystallization process in which grain growth occurs with nucleation, and the nucleation rate decreases with the progress of the grain growth process. This is fairly consistent with the crystallization behavior of the Cu/a-Si bilayer recording film during nonisothermal annealing, where the Cu$_3$ Si phase pre-
precipitates first and then acts as the nucleation sites for the subsequent crystallization of \(a\)-Si.

It should be noted that the heating rate applied on the Cu/\(a\)-Si bilayer recording film during recording by a high power pulsed laser, is much higher than that under thermal annealing so that the crystallization characteristics might be different. Figure 5(a) shows the TEM images of a Cu/\(a\)-Si bilayer and \(a\)-Si single-layer after irradiation by a 399 nm blue pulsed laser with a power of 6 mW for various durations. It is seen that recording marks were formed in the Cu/\(a\)-Si bilayer recording film, whereas no structural change was observed in the \(a\)-Si single layer. Obviously, the recording power of Cu/\(a\)-Si bilayer used for the blue-ray disk was much lower than that of \(a\)-Si single layer, because of the lower crystallization temperature and activation energy with the aid of Cu-induced crystallization. As we closely examined the microstructure of the recording mark formed in the Cu/\(a\)-Si bilayer recording film, as shown in Fig. 5(b), \(\text{Cu}_3\text{Si}\) precipitates with sizes of tens of nanometers were found to be uniformly dispersed in the polycrystalline Si matrix, which was the same as the microstructure found in the Cu/\(a\)-Si bilayer recording film after thermal annealing at 500 °C for 3 min. As a result, the crystallization behavior of the Cu/\(a\)-Si bilayer recording film under pulsed laser annealing could reasonably be considered to be similar to that under thermal annealing, that is, the \(\text{Cu}_3\text{Si}\) phase would precipitate first and serve as the nucleation sites for the following crystallization of the remaining amorphous Si. It is worthy to mention that the rapid solid phase crystallization of \(a\)-Si with a thin Cu layer under pulsed laser annealing is different from the melt crystallization of \(a\)-Si under high power pulsed laser irradiation. This is because the laser energy density applied in this study is only high enough for the crystallization of the Cu/\(a\)-Si bilayer, but not enough for the crystallization or melting of pure \(a\)-Si.

To further understand the crystallization kinetics of the Cu/\(a\)-Si bilayer recording film under pulsed laser annealing, the as-deposited Cu/\(a\)-Si bilayers were irradiated by a blue pulsed laser with powers of 6, 8, and 10 mW for 40 ns, and the reflectivity variations were monitored in real time, as shown in Fig. 6(a). Clearly, typical S-shaped transformation curves were also found in all Cu/\(a\)-Si bilayer recording films under pulsed laser annealing. As irradiated by a pulsed laser, the Cu/\(a\)-Si bilayer recording film would exhibit a rapid increase in reflectivity once the crystallization of \(a\)-Si was triggered, and the reflectivity of the recording film would reach a saturated value 90 ns after the irradiation, when the crystallization process was complete. The saturated value was found to increase with the laser power because the temperature profile of the laser spot with a higher laser power is higher than that with a lower laser power, so that the crys-
tallization area in the laser spot with a higher laser power will be larger than that with a lower laser power, leading to a higher saturated reflectivity. Higashi and Sameshima have also reported a similar transient reflectivity variation in the pure a-Si film irradiated by a pulsed laser with a laser energy density beyond the crystallization threshold. However, the increase of the reflectivity in their experiment was due to the melting of Si film, not the solid phase crystallization. The reaction exponent \( \alpha \) which was determined from the \( \ln(-\ln(1-X)) \) versus \( \ln(t-t_0) \) plots, as shown in Fig. 6(b), was found to vary from 1.2 to 1.4, indicating the crystallization of a-Si with a thin Cu underlayer under pulsed laser annealing was a grain-growth-controlled process associated with instantaneous nucleation. It appears that the crystallization behavior of the Cu/a-Si bilayer under pulsed laser annealing at ultrafast heating rate is slightly different from the case under thermal annealing at a much lower heating rate where grain growth occurs with nucleation. That is probably because less time is available for the nucleation of Cu3Si phase before the crystallization of a-Si commences.

To estimate the activation energy for crystallization of the Cu/a-Si bilayer recording film under pulsed laser annealing, temperature distribution at the recording layer is calculated using a two-dimensional finite difference method to solve the heat transfer equation, which can be expressed as

\[
C_p \frac{\partial T}{\partial t} = k \nabla^2 T + Q.
\]

Here \( C_p \) is the specific heat, \( k \) is the material’s thermal conductivity, and \( Q \) is the heat source. Light absorption by the recording film is assumed to be the main source. The heat source is obtained from the results of the optical characteristic simulation by considering multiple reflections. The laser beam intensity is described by the Gaussian distribution

\[
I(x,y) = \frac{P}{(\pi r_0^2)} \exp\left[-(x^2 + y^2)/r_0^2\right],
\]

where \( P \) is the instantaneous laser beam power and \( r_0 \) is the 1/e^2 radius of the Gaussian beam. Thus the heat source term \( Q \) can be calculated as the summation of the product of energy absorbance and light intensity at each mesh. Table I lists the optical and thermal properties of the materials used in our simulation. Here the thermal conductivity of Cu thin film is assumed to be one tenth of the value for bulk material. The simulated temperature profiles show that the a-Si layer will be heated to a saturation temperature immediately after the laser pulse is turned on. The saturation temperatures at the center of the laser spot on a-Si layer are calculated to be 543, 724, and 905 °C, respectively, as the blue laser pulses with powers of 6, 8, and 10 mW are applied for 40 ns. Considering the slope in the acceleration regime of the transformation curve in Fig. 6(a) as the crystallization velocity, the Arrhenius plot of crystallization velocity versus reciprocal temperature for the Cu/a-Si bilayer under blue pulsed laser annealing, as shown in Fig. 7, yields an activation energy of ~0.22 eV. It is seen that the activation energy for crystallization of the Cu/a-Si bilayer under pulsed laser annealing is nearly one order of magnitude lower than that under thermal annealing. This may be explained by the explosive crystallization of a-Si by mechanical impact with a high power pulsed laser. As the Cu/a-Si bilayer gets irradiated by a high power pulsed laser, the covalent Si-Si bonds in the irradiated region would be broken, and the temperature of the Cu/a-Si bilayer would have risen instantaneously above the threshold temperature for solid phase explosive crystallization. The formation of the Cu3Si phase prior to the crystallization of a-Si lowers system free energy and provides the nucleation sites for the subsequent explosive crystallization of a-Si, resulting in a much lower activation energy.

### IV. CONCLUSIONS

We have studied the crystallization kinetics of the Cu/a-Si bilayer recording film under thermal and pulsed laser annealing. It is confirmed that inserting a thin Cu metal layer can effectively reduce the crystallization temperature and activation energy for crystallization of a-Si. For both thermal and pulsed laser annealing, Cu3Si precipitates with sizes of tens of nanometers were formed prior to the crystallization of a-Si, and served as the nucleation sites for subsequent crystallization of the remaining amorphous Si, which resulted in a crystallization process governed by grain growth. The activation energy for crystallization of the Cu/a-Si bilayer under pulsed laser annealing is nearly one order of magnitude lower than that under thermal annealing, which might be due to the explosive crystallization of a-Si by mechanical impact with a high power pulsed laser.

### Table I. Optical and thermal properties of PC substrate and Cu and a-Si thin films.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Refractive index</th>
<th>Extinction coefficient</th>
<th>( C_p ) (J/cm^3/K)</th>
<th>k (J/cm K s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC substrate</td>
<td>1.46</td>
<td>0</td>
<td>1.7</td>
<td>0.0022</td>
</tr>
<tr>
<td>Cu thin film</td>
<td>1.205</td>
<td>2.14</td>
<td>4.436</td>
<td>0.4</td>
</tr>
<tr>
<td>a-Si thin film</td>
<td>5.183</td>
<td>1.956</td>
<td>1.733</td>
<td>0.0243</td>
</tr>
</tbody>
</table>
ACKNOWLEDGMENTS

This work was sponsored by the National Science Council of the Republic of China under Grant No. NSC91-2216-E005-023. The authors would like to thank Shun-Te Cheng and Dr. Song-Yeu Tsai from ITRI for static testing and Edward Young for reviewing the manuscript.

23 S. Adach, Optical Constants of Crystalline and Amorphous Semiconductors (Kluwer Academic, Massachusetts, 1999).