Growth of Ti-Based Interface Layer in Cu(Ti)/Glass Samples

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Cu(Ti) alloy films with low-resistivity and excellent-adhesion have been successfully prepared on glass substrates. To gain further resistivity reduction and adhesion strength, growth of a Ti-based interface layer was investigated using Rutherford backscattering spectrometry (RBS) in the present study. Cu(0–5 at%Ti) alloy films were deposited on glass substrates and subsequently annealed in vacuum at 400–600°C for 0.5–24 h. Results were compared with those for samples on SiO2 substrate previously obtained. Ti peaks were obtained in RBS spectra only at the interfaces for both Cu(Ti)/glass and Cu(Ti)/SiO2 samples. Molar amounts of Ti atoms segregated to the interfaces (n) were estimated from Ti peak areas. The m values estimated from the slopes of the log n versus log t lines were almost similar for all the samples (m = 0.10–0.12), suggesting that growth of the Ti-based interface layers was controlled by a similar mechanism. The activation energy of the Cu(Ti)/glass samples was similar to that of the Cu(Ti)/SiO2 samples, while a pre-exponential factor (Z) of the Cu(Ti)/glass samples was approximately half of the value of the Cu(Ti)/SiO2 samples. The Z value shows the frequency with which the Ti atoms meet oxygen in the glass substrates. Impurities in the glass substrates lowered the frequency. These factors lead to the conclusion that growth rate of the Ti-based interface layers on glass substrates was slower than that on SiO2. The Ti-based interface layer growth was also influenced by microstructure of Cu(Ti) alloy films formed on the glass substrates. Columnar grains in the Cu(Ti) alloy films were seen to enhance Ti segregation. However, an equiaxed zone above the interface retarded Ti diffusion to the interface, leading to lack of Ti atoms for the reaction.

Keywords: copper titanium alloy film, titanium segregation, Rutherford backscattering spectrometry, glass substrate

1. Introduction

As the size and resolution of thin film transistor liquid crystal displays (TFT-LCDs) increase, copper is becoming an attractive candidate for the gate and interconnect materials to replace Mo(W) and Al(Nd) alloys. Copper has been evaluated for use in TFT-LCDs gate electrodes and the Cu-based TFT production process includes formation of a Cu/Mo bilayer gate electrode using wet etching of a sputter-deposited Cu/Mo bilayer. The process addresses Cu-related issues such as wet-etching difficulties and poor adhesion to dielectrics. Extensive efforts have been made to improve these Cu-related issues, for example, developing processes for production of Cu/metal bilayers such as Cu/Cr8, Cu/Mo,7 Cu/Ti,8 and Cu alloys such as Cu(Cr)9 and Cu(In).10,11 Similarly, Cu alloys such as Cu(Ti)12–15 and Cu(Mn)16,17 were investigated to prepare a thin barrier layer on dielectric/Si substrates for ultra-large scale integrated devices, leading to low resistivity and high adhesion. Supersaturated Cu(Ti) alloy films deposited on dielectric layers such as SiO2, SiN, SiCO, SiCN, and SiOCH with low dielectric constants (low-k) were annealed at elevated temperatures, and thin Ti-rich layers were formed at the film surface and interface between the film and all the dielectric layers.13,14 Such a Ti-based self-formed barrier formation using a Cu(Ti) alloy was applied to seed the Cu metallization on glass substrates in a previous study.18 Low-resistivity and excellent-adhesion Cu(Ti) alloy films have been successfully prepared on glass substrates. To gain further resistivity reduction and adhesion strength, growth of a Ti-based interface layer was investigated using Rutherford backscattering spectrometry (RBS) in the present study.

2. Experimental Procedures

Cu(0–5 at%Ti) alloy films were deposited on glass substrates (Eagle2000, Corning, Inc.) by a radio frequency magnetron sputtering technique. Prior to film deposition, dust on the substrate surface was blown off using nitrogen gas. For comparison, results of Cu(5 at%Ti) alloy films deposited on SiO2/Si substrates were derived from a previous study. The SiO2 layer was grown on the Si substrate by oxidation. The base pressure prior to deposition was approximately 1 × 10−6 Pa, and the sputtering power and working pressure were kept at 300 W and about 1 Pa, respectively. The substrate holder was placed 100 mm above a target. To prepare the Cu(Ti) alloy films, small rectangular Ti plates were mounted on a Cu target. The purities of the Cu target and the Ti plates were 99.99% and 99.9%, respectively. The film thicknesses were measured using transmission electron microscopy (TEM) and RBS: the typical thickness of the Cu(Ti) alloy films was controlled to approximately 300 nm. The samples were annealed in ultrahigh vacuum (UHV) isothermally at 400°C to 600°C for 0.5 h to 24 h. The electrical resistivity of the Cu(Ti) alloy films was measured by a four-point probe method. The film microstructures were analyzed by TEM. The Ti segregation to the interface was investigated by RBS. Ti segregation only at the interface was observed after the annealing in UHV. For the RBS measure-
ments, $^4$He$^{2+}$ ion beams with energy of 2 MeV were impinged perpendicularly onto the film surfaces. A detector counted each particle scattered at 170° from the direction of incidence.

3. Results and Discussion

3.1 Ti Segregation at interface between Cu(Ti) alloy films and glass substrates

Figure 1 shows RBS spectra of Cu(2.3 at% Ti)/glass samples after annealing in UHV. Ti peaks were observed only at the interfaces in all the samples. Based on a previous study, the Ti segregation at the interface indicates that Ti-based interface layers consisting of amorphous Ti oxides formed. The Ti-peak intensities increased with increasing annealing time (Fig. 1(a)) and annealing temperature (Fig. 1(b)), suggesting that the Ti-based interface layer growth increased. Similar RBS spectra were obtained in Cu(3.5 at% Ti)/glass samples after annealing in UHV (not shown here).

Figure 2 shows portions (around the Ti peaks) of the RBS spectra of Cu(2.3 at% Ti)/glass samples after annealing at 400°C for 2 h in UHV shown in Fig. 1, with calculation plots (solid line) placed upon the observed data. The calculation plots consisted of three components: Ti segregation at the interface (Gaussian curve), Ti atoms in the alloy film (error function), and a Cu edge above the Ti segregation at the interface (error function). A best fit of the calculated spectrum to the observed spectrum was obtained on the basis of various indicators such as the weighted pattern $R$ index ($R_{wp}$) and the ratio $R_{wp}/R_e$ ($= S$) where $R_e$ is the expected $R$ index. The $S$ values were in the range of 1.0 to 1.3 in all the samples, low enough to indicate an adequate model. Similarly, a small $R_{wp}$ value is attributed to sufficiently large reaction of the Ti atoms with the glass substrate. The RBS refinement processes were also conducted in Cu(Ti)/glass samples annealed at other annealing temperatures and times.

The peak area ($A$) of the Ti segregation at the interface in an RBS spectrum is the product of the total number of incident He ions ($Q$), the number of the Ti atoms in a unit of area ($N$), the scattering cross section of the Ti atom ($\sigma$), and the solid angle of the detector ($\Omega$).

![Fig. 1](image1.png)  RBS spectra of the Cu(2.3 at% Ti)/glass samples after annealing in UHV (a) at 400°C for various annealing times and (b) at various annealing temperatures for 2 h. For comparison, RBS spectra before annealing are plotted together in both (a) and (b).

![Fig. 2](image2.png) Portions (around the Ti peaks) of the RBS spectra of Cu(2.3 at% Ti)/glass samples after annealing at 400°C for 2 h in UHV shown in Fig. 1, with refinement plots (solid line) placed upon the observed data. The refinement plots consisted of three components: Ti segregation at the interface, Ti atoms in the alloy film, and a Cu edge above the Ti segregation at the interface.
A = QNσΩ. \hspace{1cm} (1)

The molar amount of Ti atoms segregated to the interface (n) was estimated by dividing the number (N) from eq. (1), above, by Avogadro’s number NA:

\[
n = \frac{N}{N_A} = \frac{A}{N_A Q} \sigma \Omega. \hspace{1cm} (2)
\]

In the present study, the A value was determined from the area under the fitted Gaussian curve. The values of Q, Ω, and σ of Ti atoms were 3.12 × 10^{13} (10 μC), 3 × 10^{-3} sr, and 6.28 × 10^{-29} m^{2} (0.628 b), respectively. The n values estimated from the obtained A values originating from the Ti atoms segregated at the interface (eq. (2)) are summarized in later sections.

### 3.2 Growth behavior of the Ti-based interface layers

Growth of the Ti-based interface layers on the glass substrate after the annealing is exhibited as n values estimated from the A values originating from the Ti atoms segregated at the interface. Plots of n versus annealing time (t) for Cu(2.3 at%Ti)/glass and Cu(3.5 at%Ti)/glass samples after annealing at 400°C are shown in Fig. 3(a). For comparison, those for Cu(5 at%Ti)/SiO\textsubscript{2} samples after annealing at 400°C obtained in a previous study\textsuperscript{15} are shown together in Fig. 3(a). The n values increased with increasing annealing time and gradually arrived at saturating values in both types of the samples. The n values for the Cu(2.3 at%Ti)/glass samples were similar to those for the Cu(3.5 at%Ti)/glass samples. This suggests that the initial Ti concentration of 2.3 at% is sufficient to continue the reaction of the Ti atoms with the glass substrates, although the Ti concentration in the alloy films decreased during the annealing. Also, a number of residual Ti atoms in the alloy films for the Cu(3.5 at%Ti)/glass samples was suggested to be larger than that for the Cu(2.3 at%Ti)/glass samples. In fact, the resistivity for the Cu(3.5 at%Ti)/glass samples was higher than that for the Cu(2.3 at%Ti)/glass samples after annealing under the same conditions. The n values for the Cu(Ti)/glass samples were lower than those for the Cu(5 at%Ti)/SiO\textsubscript{2} samples. This can be explained by the intrinsic difference between the reaction of Ti atoms with the glass substrates and that with the SiO\textsubscript{2} layers.

On the other hand, growth behavior of the Ti-based interface layers was defined by

\[
n = Z \cdot \exp(-E/RT) \cdot t^m, \hspace{1cm} (3)
\]

where Z is a pre-exponential factor and E is the activation energy for the reaction. The plots of n versus t (Fig. 3(a)) were transformed to plots of \(\log n\) versus \(\log t\) (Fig. 3(b)). The \(\log n\) values were found to be proportional to the \(\log t\) values in all the samples. The m values were estimated from the slopes of the \(\log n\) versus \(\log t\) lines, and were almost similar for all the samples (m = 0.10–0.12). The similar m values suggest that growth of the Ti-based interface layers was controlled by a similar mechanism. The m values were far lower than 0.5, suggesting that growth of the Ti-based interface layers is not controlled by lattice diffusion, but perhaps by grain-boundary diffusion with grain growth. However, as amorphous materials, the Ti-based interface layers consisting of Ti oxides have no grain boundary and no reduction of grain boundary cross-sectional area as a diffusion path during annealing, and thus the growth mechanism remains unclear.

### 3.3 Activation energies and reaction rates of the Ti-based interface layer growth

Arrhenius plots of \(\log n\) versus 1/T for the Cu(2.3 at%Ti)/glass and Cu(3.5 at%Ti)/glass samples after annealing for 2 h are shown in Fig. 4, together with those for Cu(Ti)/SiO\textsubscript{2} samples\textsuperscript{15} for comparison. The plots show a linear relationship, which suggests that the formation of the Ti-based interface layers was controlled by a thermally-activated process. Slopes of the \(\log n\) versus 1/T lines for the Cu(Ti)/glass and Cu(Ti)/SiO\textsubscript{2} samples are similar in the temperature range below 500°C. Activation energies, E, were estimated from the slopes of the \(\log n\) versus 1/T lines. The pre-
exponential factors, \( Z \), were estimated from intercepts of the slopes in the \( \log n \) versus \( \log t \) lines (Fig. 3(a)) and \( \log n \) versus \( 1/T \) lines (Fig. 4). The values of \( m \), \( E \), and \( Z \) for the \( \text{Cu}(2.3 \text{ at}\%\text{Ti})/\text{glass}, \text{Cu}(3.5 \text{ at}\%\text{Ti})/\text{glass}, \) and \( \text{Cu}(\text{Ti})/\text{SiO}_2 \) samples are summarized in Table 1, although the values of \( E \) and \( Z \) for the \( \text{Cu}(3.5 \text{ at}\%\text{Ti})/\text{glass} \) samples were unreliable due to insufficient experimental data. The \( E \) value of the \( \text{Cu}(2.3 \text{ at}\%\text{Ti})/\text{glass} \) samples was similar to that of the \( \text{Cu}(\text{Ti})/\text{SiO}_2 \) samples, while the \( Z \) value of the \( \text{Cu}(2.3 \text{ at}\%\text{Ti})/\text{glass} \) samples was approximately half of the value of the \( \text{Cu}(\text{Ti})/\text{SiO}_2 \) samples. The \( Z \) value shows the frequency with which the Ti atoms meet elemental reactants in the glass substrates. The frequency for the \( \text{Cu}(2.3 \text{ at}\%\text{Ti})/\text{glass} \) samples was lower than that for the \( \text{Cu}(\text{Ti})/\text{SiO}_2 \) samples. This can be attributed to impurities in the glass substrates. The glass substrates contain impurity elements such as 4.5 at\%Al, 2.2 at\%B, and 1.3 at\%Ca. The impurities lowered the frequency with which the Ti atoms meet oxygen in the glass substrates.

Coefficients of the reaction rate (\( Z \cdot \exp(-E/RT) \)) can be calculated as a function of annealing temperature based on the obtained values of \( E \) and \( Z \). The calculated coefficients decreased with decreasing annealing temperature as shown in Fig. 5, and those for the \( \text{Cu}(2.3 \text{ at}\%\text{Ti})/\text{glass} \) samples were lower than those for the \( \text{Cu}(\text{Ti})/\text{SiO}_2 \) samples in the calculated temperature range. The difference in growth of the Ti-based interface layers formed at the interface between the two types of samples was attributed to the difference in the \( Z \) values as shown in Table 1. The growth of the Ti-based interface layers for the \( \text{Cu}(\text{Ti})/\text{glass} \) samples was not sensitive to annealing temperature compared with that for the \( \text{Cu}(\text{Ti})/\text{SiO}_2 \) samples, suggesting a large process window.

### 3.4 Growth of the Ti-based interface layers influenced by microstructure of Cu(Ti) alloy films

In a previous study, we reported that some \( \text{Cu}(\text{Ti})/\text{glass} \) samples did not show resistivity reducing to such low resistivity as around 2.8 \( \mu \Omega \text{cm} \) after annealing at 400°C in conventional vacuum.\(^{10} \) This could be attributed to a thick and fine equiaxed zone on the glass substrates, leading to pinning of the Ti atoms at the grain boundary. In the present study, the \( n \) values were estimated from RBS analyses, and clarified the effect of microstructure of \( \text{Cu}(\text{Ti}) \) alloy films on the growth of the Ti-based interface layers. Figure 6 shows dependence of resistivity and the \( n \) values on annealing temperature for the \( \text{Cu}(0\text{~at}\%\text{Ti})/\text{glass} \) samples after annealing at 400°C in UHV. Sample sets A and B were typical examples for the samples reducing and not reducing to such low resistivity as around 6 \( \mu \Omega \text{cm} \), respectively (Fig. 6(a)). Preparation of sample set A followed the experimental procedure. Sample set B was prepared using a different sputter equipment with direct current and/or under higher base pressure than \( 1 \times 10^{-6} \text{ Pa} \) prior to deposition. With increasing annealing temperature, such difference in resistivity reduction became obvious: resistivity decreased to 2.8 \( \mu \Omega \text{cm} \) for sample set A, but to 5 \( \mu \Omega \text{cm} \) for sample set B after annealing.
The difference can be attributed to difference in the $n$ values in sample sets A and B. In sample set A, relatively large amount of Ti atoms segregated to the interface and the value continued to increase even after 5 h. In contrast, the amount of Ti atoms segregated to the interface was relatively small in sample set B, and the value did not increase with increasing annealing time.

To identify such difference in sample sets A and B, growth behavior of the Ti-based interface layers represented by the values of $m$, $E$, and $Z$ was investigated by RBS measurements. Figure 7 shows plots of $\log n$ versus $\log t$ (annealing at 400°C) and arrhenius plots of $\log n$ versus $1/T$ (annealing for 2 h) for sample sets A and B after annealing in UHV. The $n$ values of sample set A were always higher than those of sample set B in all annealing time and temperature ranges. The values of $m$, $E$, and $Z$ estimated from Fig. 7 are summarized in Table 2. All the values for sample set A were larger than those for sample set B. The lower $m$ value of sample set B suggests that diffusion path of grain boundary decreased significantly. However, significant grain growth was not observed in cross-sectional TEM images (not shown here), and thus the Ti diffusion was retarded by some other mechanism. The lower $E$ value suggests that amounts of the

<table>
<thead>
<tr>
<th>Sample set</th>
<th>$m$</th>
<th>$E$ (kJ/mol)</th>
<th>$Z$ (mol/m²/h⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.10</td>
<td>43</td>
<td>0.90</td>
</tr>
<tr>
<td>B</td>
<td>0.020</td>
<td>18</td>
<td>0.0064</td>
</tr>
</tbody>
</table>
Ti atoms were insufficient to continue to react with the glass substrates. In a previous study, small amount of Ti atoms in Cu(1 at%Ti) alloy films decreased the E value compared with the other initial Ti concentrations. In the present case, the initial Ti concentration was sufficient to continue the reaction, and thus Ti diffusion to the interface was suppressed by some other mechanism. The lower Z value shows that the encounter rate between Ti and O atoms decreased. This is also due to lack of the Ti atoms for the reaction at the interface.

To identify the cause of suppression of Ti diffusion to the interface, location of the Ti atoms remaining in the Cu(Ti) alloy films was clarified. To identify the location, resistivities of the Cu(0~5 at%Ti)/glass samples after annealing in UHV for 0.5~24 h at 400~600°C were plotted with respect to residual Ti concentration in the Cu(Ti) alloy films (Fig. 8). The residual Ti concentration was estimated by subtracting the Ti concentration segregated at the interface determined by RBS measurements from the initial Ti concentration determined by SEM/EDX. The concentrations determined by RBS were calculated using $\sigma$ corrected with the ratio of the count at surface to the count at interface in the Cu portion of the RBS spectrum, and those determined by SEM/EDX were corrected using concentrations obtained by a mass spectroscopy. Figure 8 shows that there was no obvious difference in relationship between resistivity and concentration of the residual Ti atoms in sample sets A and B. The obtained resistivities were lower than the sum (a broken line) of resistivities for pure Cu thin films (a solid line) and resistivity increases due to impurity scattering (a broken triangle). The resistivities for pure Cu thin films as-deposited and annealed in UHV at 400°C for 2~3 h were obtained to be 2.4~2.5μΩcm. The resistivity increase due to Ti impurity atoms has been obtained to be 10μΩcm/1 at%Ti in the as-deposited Cu(Ti) alloy films with Ti concentrations of 0.5~4 at%.

Figure 9 shows cross-sectional TEM images of typical microstructures of the as-deposited sample sets A and B. Sample set A shows columnar grains in more than half of the upper part of the Cu(Ti) alloy film and thin equiaxed zone was observed between the columnar grains and glass substrates (Fig. 9(a)). In contrast, sample B shows a thicker equiaxed zone, as shown in Fig. 9(b). In sample set A, the equiaxed zone had disappeared after annealing for 30 min, and columnar grains grew from the interface to the surface. In sample set B, fine columnar grains remained even after annealing for 180 min. Thus, the difference in thickness of the equiaxed zone above the glass substrates between the
as-deposited samples A and B influenced the Ti diffusion to the interface. The grain boundaries around the equiaxed grains formed many triple points, which acted as roadblocks preventing the Ti diffusion from moving directly to the interface. The Ti atoms might be gradually pinned at the grain boundary due to oxygen penetration through the grain boundary during annealing, in which case the Ti contamination at the grain boundary would lead to prevention of further grain growth. The smaller volume fraction of equiaxed grains in the as-deposited samples is a key for the faster Ti segregation to the interface and resistivity reduction to such low resistivity as 2.8 μΩcm.

4. Conclusions

For systematic investigation of the growth of the Ti-based interface layers in annealed Cu(Ti)/glass samples to gain further resistivity reduction and adhesion strength, the RBS technique was employed. Cu(0–5 at%Ti) alloy films were deposited on glass substrates, and subsequently annealed in UHV at 400–600°C for 0.5–24 h. Ti peaks were obtained in RBS spectra only at the interfaces for both Cu(Ti)/glass and Cu(Ti)/SiO₂ samples. Molar amounts of Ti atoms segregated to the interfaces were estimated from Ti peak areas.

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