



## The Inhibition of Silver Agglomeration by Gold Activation in Silver Electroless Plating

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In Ag electroless plating, Ag agglomeration has been the obstacle to obtain thin Ag films. The crystallographic misfit between the substrate and Ag can accelerate Ag agglomeration. In this paper, Au, whose crystallographic characteristics are similar with those of Ag, is used as the activation material. As a result, the Ag layer was deposited in the form of layer-by-layer growth. Therefore, Ag film electrolessly deposited on a substrate activated by Au can be used to manufacture the interconnections in microelectronic devices. In this experiment, the resistivity of the Ag film was measured to 2.5  $\mu\Omega$  cm, which was decreased to 1.95  $\mu\Omega$  cm by the annealing process.

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With decreasing feature sizes in integrated circuits, the availability of interconnection material showing low resistivity has become essential.<sup>1,2</sup> In addition, when material with low resistivity is used, the thickness of the interconnections can be reduced, which makes the fabrication of the devices easier. Therefore, due to the lowest bulk resistivity of 1.6  $\mu\Omega$  cm, Ag has high potential for use in microelectronic devices.

In this paper, electroless plating technology was used to deposit Ag film. Because electroless plating technology has the advantage of enabling uniform film deposition over a large substrate area, it can be used to manufacture the interconnections required for thin-film transistor—liquid crystal display (TFT-LCD).<sup>3</sup> Recently, Ag electroless plating has been the subject of intensive research,<sup>4-11</sup> but there is at least one serious problem which remains to be resolved. During Ag electroless plating on a surface activated by Pd or Ag, the deposited Ag is agglomerated together. Therefore, it is difficult to form a thin Ag film by electroless plating. In order to resolve this problem, it was attempted to form Ag-W species.<sup>8-10</sup> However, because impurity is the main source of high resistivity, it is essential that only Ag is deposited.

In this experiment, a new activation material, Au, was attempted as the activation material for Ag electroless plating. Traditionally, Pd has been used as the activation material in Cu<sup>3,12,13</sup> and Ag<sup>8,10</sup> electroless plating. However, as shown in Table I,<sup>14</sup> there is a lattice mismatch of 5% between Pd and Ag. This fact can make the adhesion between Ag and Pd aggravate. Therefore, the substitution of the traditional activation material by Au is expected to improve the adhesion between Ag and the substrate.

It is known from Table I<sup>14</sup> that Ag has the same face-centered cubic (fcc) crystal structure as Au. Also, the lattice constants of the two metals have almost identical values. These characteristics improve the bonding between Ag and Au, which may prevent agglomeration of the Ag. In addition, the resistivity of Au, 2.4  $\mu\Omega$  cm, is relatively low. Therefore, the presence of Au in the interconnection has little influence on their resistivity. Table II<sup>15</sup> shows the reduction potentials of various metals. Among them, Au has the highest reduction potential among conventional metals. This indicates that Au can be favorably deposited on a TiN diffusion barrier by means of a displacement reaction. Moreover, because of the strong resistance of Au against oxidation, no metal oxide is generated at the interface between Au and Ag. These factors can help to avoid the problem of Ag agglomeration.

### Experimental

A blanket wafer whose structure was TiN(10 nm)/Ti(15 nm)/Si wafer was used as the substrate for Ag electroless plating. TiN layer

had been deposited to prevent metal from diffusing into the electronic devices. Because TiN is oxidized naturally and Ti oxide is an insulator, it has to be removed by immersion in 1% HF solution for 10 min.<sup>12</sup> Deposition of the activation metal is necessary to perform Ag electroless plating on the substrate. In this experiment, Pd and Au were used as the activation metals. Each activation solution was optimized for Ag electroless plating as follows. The Pd activation solution was composed of 0.1 g/L PdCl<sub>2</sub>, 3 mL/L 35% HCl, and 5 mL/L 50% HF. The Au activation solution was composed of 0.2 g/L AuCl<sub>3</sub> and 5 mL/L 50% HF.

Ag electroless plating can be carried out on the activated substrate. The Ag electroless plating solution contained 6.5 g/L AgNO<sub>3</sub>, 500 mL/L 28% NH<sub>4</sub>OH, 28 g/L CoSO<sub>4</sub> · 7H<sub>2</sub>O, 50 g/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and 0.025 g/L Mg(OH)<sub>2</sub>. In this electrolyte, Co ion was used as the reducing agent and ammonium salt was added to form the complex of Ag ion with Co ion.<sup>7</sup> Finally, the deposited Ag film was annealed at 350°C for 30 min. An annealing process was carried out in vacuum condition with N<sub>2</sub> gas purging.

To measure the large-scale surface roughness of deposited Ag, the reflectivity of the surface was measured using a laser beam with a wavelength of 650 nm. X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), atomic force microscopy (AFM), Auger electron spectroscopy (AES), and field emission scanning electron microscopy (FESEM) were used to analyze deposited substrate.

### Results and Discussion

Metal activation was performed after Ti oxide etching using a 1% HF solution. In the activation reaction, electrons generated by the oxidation of the substrate cause the activation metal ions to be reduced on the substrate surface.<sup>16</sup> It was known from XPS analysis that Pd and Au species were deposited on the substrate after the activation step (Fig. 1). The reduction potential of Ti is -1.63 V vs. normal hydrogen electrode (NHE), which was much lower than that of every metal used as the activation metal in this experiment (Table II). Therefore, all displacement reactions of Pd and Au on TiN layer occur spontaneously.

Table I. Material property of metals.<sup>14</sup>

Element	Crystal structure	Lattice constant (nm)	Resistivity ( $\mu\Omega$ cm)
Cu	fcc	0.362	1.7
Pd	fcc	0.389	10.7
Pt	fcc	0.392	10
Ru	hcp <sup>a</sup>	0.271	7.1
Ag	fcc	0.409	1.6
Au	fcc	0.408	2.4

<sup>a</sup> Hexagonal close packed.

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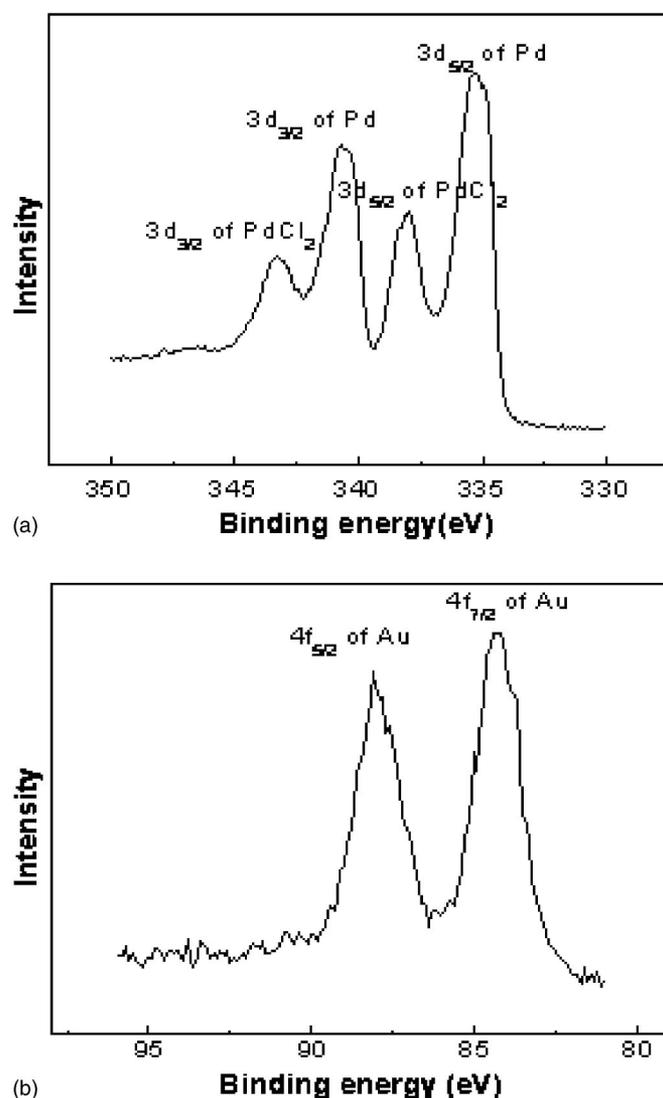
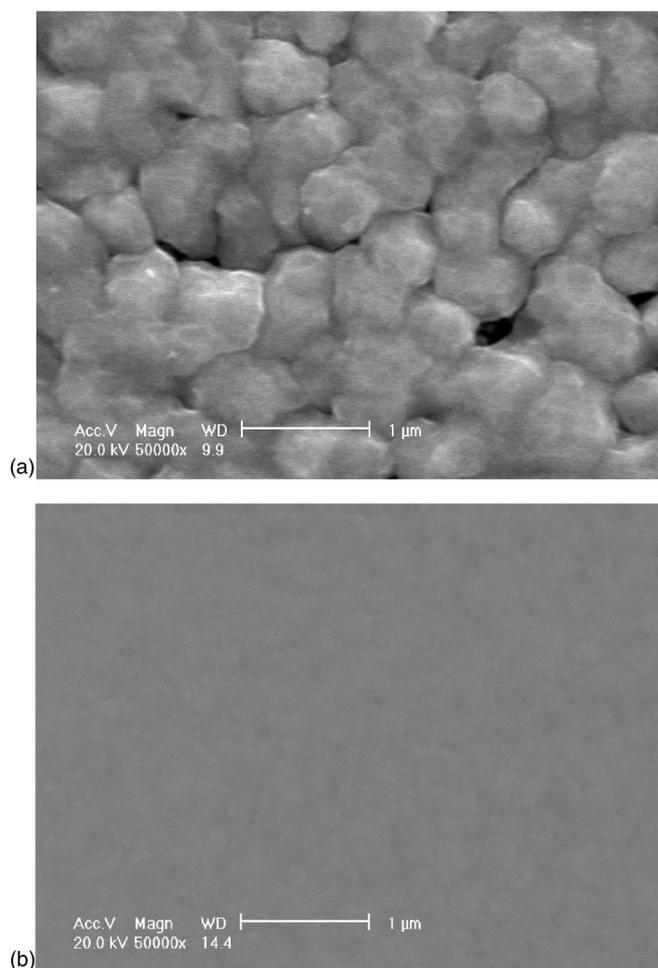
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**Table II. Reduction potential of metal ion.<sup>15</sup>**

Reaction	Reduction potential
$\text{Ag}^+ + e \rightleftharpoons \text{Ag}$	$E^0 = 0.7991 \text{ V vs. NHE}$
$\text{Au}^+ + e \rightleftharpoons \text{Au}$	$E^0 = 1.83 \text{ V vs. NHE}$
$\text{Au}^{3+} + 2e \rightleftharpoons \text{Au}^+$	$E^0 = 1.36 \text{ V vs. NHE}$
$\text{Pd}^{2+} + 2e \rightleftharpoons \text{Pd}$	$E^0 = 0.915 \text{ V vs. NHE}$
$\text{Ru}^{3+} + 3e \rightleftharpoons \text{Ru}$	$E^0 = 0.6 \text{ V vs. NHE}$
$\text{Cu}^+ + e \rightleftharpoons \text{Cu}$	$E^0 = 0.518 \text{ V vs. NHE}$
$\text{Cu}^{2+} + 2e \rightleftharpoons \text{Cu}$	$E^0 = 0.339 \text{ V vs. NHE}$
$\text{Cu}^{2+} + e \rightleftharpoons \text{Cu}^+$	$E^0 = 0.161 \text{ V vs. NHE}$

Following the activation step, Ag electroless plating was carried out for 10 min. From the FESEM analysis (Fig. 2a), it was found that the Ag layer deposited on Pd was agglomerated. The agglomerated Ag layer lowered the reflectivity of the laser beam by 16%. Even though the Ag electrolessly plated for 10 min did not form a completely continuous film, it reduced the sheet resistance considerably.

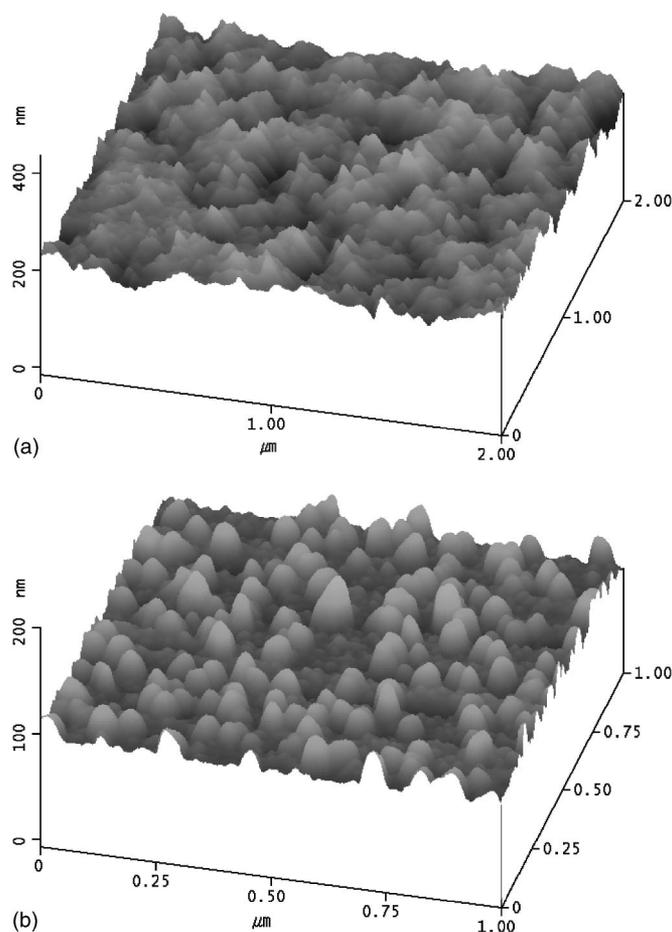
In contrast, it was remarkable that Ag species deposited on Au formed perfect film without agglomeration (Fig. 2b). The reflectivity of the deposited Ag film was 7% better than that of a commercially

**Figure 1.** XPS spectra of (a) Pd- and (b) Au-activated surface.**Figure 2.** Top FESEM images of Ag species deposited on substrate activated by (a) Pd and (b) Au.

produced mirror. Ag film deposited for 10 min on the substrate activated by Au showed a thickness of 170 nm and a surface roughness of 15 nm (Fig. 3a). The surface roughness of the substrate activated by Au was 7.9 nm, which indicated that the surface roughness was not substantially increased by Ag electroless plating (Fig. 3b).

To obtain a nonagglomerated Ag film on Pd-activated substrate,  $\text{PdCl}_2$  concentration in Pd activation solution was changed from 0.1 to 0.4 g/L. However, Ag agglomeration always occurred, regardless of  $\text{PdCl}_2$  concentration. Meanwhile, the surface roughness of Ag film was increased when  $\text{AuCl}_3$  concentration was increased to 0.5 g/L, but Ag agglomeration was not generated. It is well known in electroless plating that rough surface is obtained when using a roughly activated surface in conjunction with a high concentration of the metal species.<sup>12</sup> Therefore, the activation material rather than the activation state is the key factor in preventing Ag agglomeration.

Metal is deposited on foreign substrate via 3 different deposition mechanisms: Volmer-Weber growth mode (3D island formation), Frank-van der Merwe growth mode (layer-by-layer formation), and Stranski-Krastanov growth mode (3D island formation on top of predeposited 2D overlayers). The most important parameters determining the deposition mechanism are the metal-substrate binding energy and the crystallographic misfit.<sup>17</sup> In order for film formation to proceed via the process of layer-by-layer growth, the binding energy between the substrate and the deposited metal must be higher than that in the deposited metal, and the crystallographic misfit between the substrate and deposited metal must be small.



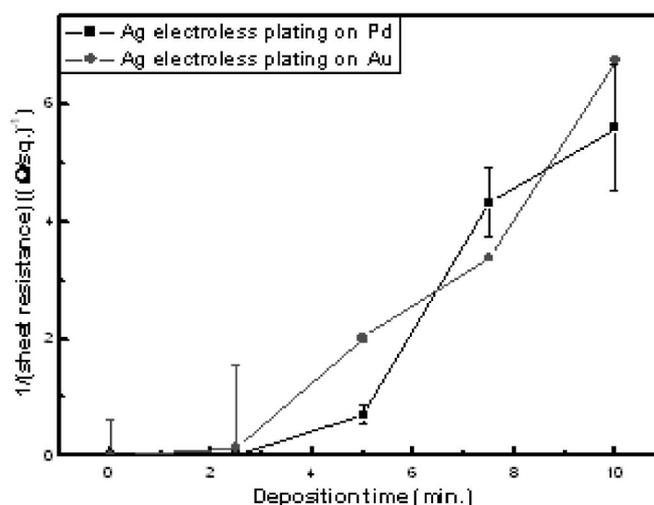
**Figure 3.** AFM images of (a) Ag-deposited surface on substrate activated by Au and (b) Au-activated surface.

While Ag-Ag binding energy is 160.3 kJ/mol, Ag-Au binding energy is 202.9 kJ/mol.<sup>18</sup> As shown in Table I, Ag has the same fcc crystal structure as Au. Also, the lattice constants of two metals have almost identical values. Therefore, Ag film can be deposited in layer-by-layer growth mode without agglomeration, when Ag is plated on a substrate activated by Au.

In the case of Pd, Pd has the same fcc crystal structure as Ag. However, the lattice constant of Pd is smaller by 5% than that of Ag, and Ag-Pd binding energy is 185 kJ/mol.<sup>19</sup> Lattice mismatch and weak binding energy between Ag and Pd result in Ag agglomeration.

The incubation time was measured to determine at which time Ag film formed. The incubation time can be obtained by measuring the sheet resistance as a function of the deposition time. The reciprocal of the sheet resistance had a linear relationship with the deposition time, 2.5 min after the deposition of Ag (Fig. 4). In the case of Pd activation, however, the incubation time was found to be 4.4 min. In other words, Au activation is more favorable to the formation of Ag film by electroless plating than Pd activation.

The amount of activated Au in the Ag film was low enough for it not to be detected by AES analysis (Fig. 5). Moreover, no impurities were detected in deposited Ag film. Therefore, the resistivity of Au in the interface does not pose a serious problem. Nevertheless, the resistivity of the Ag film deposited for 10 min on a substrate activated by Au was found to be 2.5  $\mu\Omega$  cm. This value is much higher than the bulk resistivity of Ag, 1.59  $\mu\Omega$  cm. The resistivity of film is affected by grain boundary and defect as well as impurities.<sup>20,21</sup> The full width at half maximum (fwhm) of the Ag(111) peak was measured to be 0.0049 in Fig. 6. From the Scherrer formula,<sup>22</sup> the

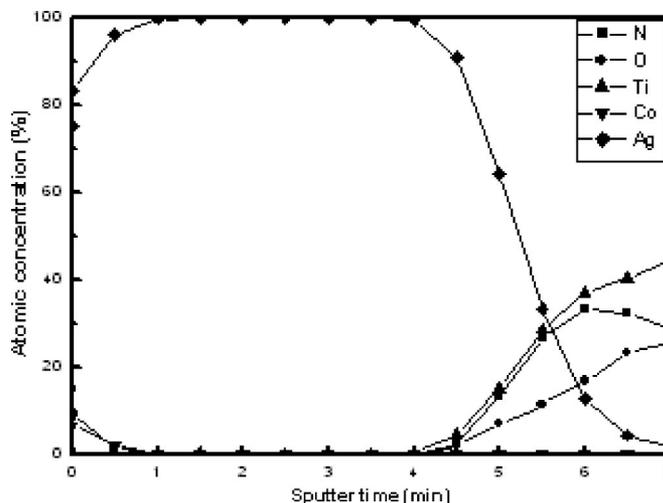


**Figure 4.** Incubation time measurement from Ag electroless plating on substrate activated by Au and Pd.

average Ag(111) grain size was calculated to be about 30 nm. Therefore, grain boundary scattering in Ag film mainly contributed to the increase in the resistivity of film.

This problem could be relieved through the annealing process, which resulted in the resistivity of the Ag film being decreased to 1.95  $\mu\Omega$  cm. The annealing process improved the adhesion property as well as the resistivity. In the 3M tape test, the annealed Ag film deposited on Au showed good adhesion.

As shown in the results of the XRD analysis in Fig. 6, the crystal structure of the Ag film deposited on the Au activated surface was superior. Grain size of 30 nm is comparable to the value of 34 nm that is found for Ag deposited on a Pd-activated surface. In principle, the average metal grain size increases during annealing in terms of agglomeration.<sup>23</sup> This phenomenon results from the surface diffusion that occurs at high temperature.<sup>24</sup> In this paper, however, Ag agglomeration was generated on the Pd-activated surface by a Volmer-Weber growth mode mechanism. Therefore, the activation metal did not have any effect on the average grain size.



**Figure 5.** AES spectra of Ag film deposited for 10 min on substrate activated by Au.

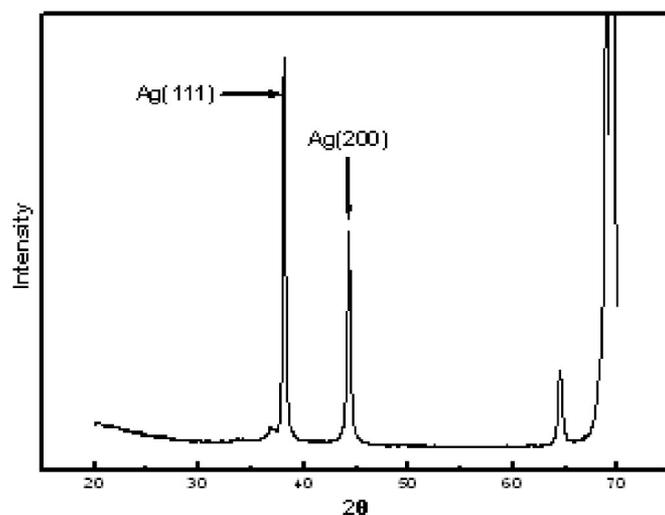


Figure 6. XRD pattern of Ag film deposited for 10 min on substrate activated by Au.

### Conclusion

Due to the intrinsic crystallographic misfit between Ag and Pd, when Ag is deposited on Pd it is agglomerated together. However, Au prevents the electrolessly deposited Ag from becoming agglomerated, because Ag-Au binding energy is higher than Ag-Ag binding energy and the crystallographic characteristics of Ag are similar to those of Au. As a result, a thin Ag film can be obtained, which can be used for the interconnections in microelectronic devices. The Au activation method reduces the surface roughness of Ag and the incubation time of Ag electroless plating. The resistivity of Ag film was measured to  $2.5 \mu\Omega \text{ cm}$ , which was decreased to  $1.95 \mu\Omega \text{ cm}$  as a result of the annealing procedure. Therefore, Au activation is essential in order to obtain a nonagglomerated Ag film by electroless plating.

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