Structural and Morphological Study of Silver Electrodeposits

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The structure and morphology of silver deposits obtained from 5 types of electroplating baths under predetermined optimal electrodeposition conditions have been studied. The deposits were formed from solutions: (a) 0.2 M KAg(CN)2 + 0.5 M KCN + 0.2 M KOH; (b) 0.2 M KAg(CN)2 + 2 M KCNS + 1 M K2CO3; (c) 0.13 M KAg(CN)2 + 0.82 M KH2PO4 + 0.41 M H3BO3 + 0.15 M K2CO3 + 0.69 M KOH; (d) 0.2 M AgNO3 + 2.5 M NaCN; (e) 0.3 M AgNO3 + 2 M Na2SO3. The obtained silver coatings as well as metallic silver were polycrystalline and nanocrystalline (the values of grain size were 36.9 – 56.5 nm). The peak broadening for electrodeposits is defined mainly by grain sizes whereas in metallic Ag one is governed by both grain sizes and microstrains. The deposits obtained from the baths in which thiocyanate or sulfite Ag(I) complexes were a source of silver contain all possible textures like in metallic silver, whereas deposits obtained from the baths in which Ag(CN)2 complexes were a source of Ag(I) does not contain texture (220) or corresponding peak is negligibly low. The values of lattice parameter and interplanar distance are in the range 34.3 nm to 80.8 nm.

Keywords: silver electroplating, electrodeposition, nanostructure, XRD, STM.

1. INTRODUCTION

The integrated circuits can be made smaller than 0.13 µm when using copper (Cu) as the interconnect material. Before, interconnects were made with other materials such as aluminium. In the sub 0.13 µm generation integrated circuits, copper will completely replace aluminum as the new interconnect material due to its favorable electrical conductivity (1.7 µΩ cm) and superior resistance to electromigration [1]. Note, the specific resistivity data corresponds to bulk material not for thin film layers. In the last case that data may vary from the bulk value dependently of their thickness [2]. Chips with more conductive Cu interconnect will operate consuming less power and at the significantly higher speeds due to decreased resistance-capacitance coupling delay. Silver is a very promising candidate for a new interconnects material because of its innate characteristics of having the lowest resistivity (1.6 µΩ cm) of all known common materials. Therefore, silver demonstrates attractive possibilities for application in microelectronics industry, e.g. for metals and alloys metallization [3 – 6] or for deposition on the barrier layers for ULSI applications [7 – 10], nanowires formation [11].

Structure and morphology govern a functionality of electrodeposits, and depend mainly on the kinetic parameters of the deposition process, and the deposition overpotential or current density, i.e. on the crystallization conditions. Obviously, the crystallization conditions might be different in various types of electroplating baths. The aim of present work is to examine morphology and structure of silver electrodeposits obtained from various kinds of baths under predetermined optimal electroplating conditions.

2. EXPERIMENTAL

X-ray diffraction (XRD) analysis was performed for the characterization of electrodeposited coatings. Ni filtered Cu–Kα1 radiation (30 kV and 30 mA, λ = 1.54056 Å) was used at a continuous scan speed of 0.02°/2θ s⁻¹. For most precise θ values for peaks and line broadenings determination the routines of the peak fitting using Gaussian- or Lorenzian-type functions were performed.

An STM instrument, NanoScope IIIa made by Digital Instruments, was used to examine a surface morphology and to estimate the roughness of the surfaces. The STM study was performed using the tunneling current up to 1 nA, the bias voltage – up to 300 mV, and the scanning rate of 0.9 – 2.0 Hz. The STM data obtained were further processed with computer software to produce 3-D images and to perform a roughness analysis.

Current density during experiments was controlled using a programmable galvanostat/potentiostat PI-50-1.1. Polished brass plates of working area 2 cm² were used as the substrates.

The silver electrodeposits were obtained from the following 5 different kinds of electroplating solutions based of KAg(CN)2 as a source of Ag(I) (baths 1 – 3), as well as pure non-cyanide solutions (baths 4 – 5) under following electrodeposition conditions:

1. cyanide [12]: 0.2 M KAg(CN)2 + 0.5 M KCN + 0.2 M KOH; j = 5 mA cm⁻², t = 20 °C.
2. diethyloargentate-thiocyanate (DCAT) [13 – 14]: 0.2 M KAg(CN)2 + 2M KCNS + 1M K2CO3;
3. RESULTS AND DISCUSSIONS

**XRD study.** Structural analysis of phases and other structural parameters of electroplated silver deposits and their comparisons with metallurgical silver were done using the XRD patterns that are shown in Fig. 1. The Miller indexes in the diffraction pattern were assigned to each peak based on the data presented in [16 – 17]. Evidently, the obtained silver coatings as well as metallurgical silver are polycrystalline. The ratios of intensities \( I_{hkl} \) of diffraction peaks are dependant on Ag-plating bath and are shown in Table 1. The deposits obtained from the baths in which thiocyanate or sulfite Ag(I) complexes are a source of silver contain all possible textures like in metallurgical silver, whereas deposits obtained from the baths in which Ag(CN)\(_2^–\) complexes are a source of silver (cyanide, DCAT and BPC) do not contain texture (220) (or corresponding peak is negligibly low (BPC bath)). Moreover, the textures (311) and (222) almost are absent in deposits, obtained from the BPC bath, and they consist mainly of phases (111) and (200). Metallurgical silver and electrodeposits obtained from the thiocyanate bath have preferential highest packing (111) orientation, whereas in other cases of electrodeposited silver two planes predominant, namely planes (111) and (200). Noticeable, that intensity of peak revealed to the plane (200) is highest for silver obtained from the sulfite bath, and it is almost equal to \( I_{111} \) for silver obtained from baths in which Ag(CN)\(_2^–\) is a source of silver (cyanide, DCAT and BPC baths).

As it is seen on Fig. 1, the corresponding values of \( 2\theta_{hkl} \) are different for metallurgical bath and electrodeposited silver. According to Bragg’s law, the values of \( \theta_{hkl} \) depend on the lattice parameter \( a_0 \) and inter planar spacing \( d_{hkl} \) in a following way [18]:

\[
\sin^2 \theta_{hkl} = \frac{\lambda^2}{4a_0^2}\left(k^2 + k^2 + l^2\right),
\]

and for cubic crystals:

\[
d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}},
\]

where \( \lambda \) is the X-ray wavelength (in Å); \( \theta_{hkl} \) is a Bragg angle.

These parameters obtained for metallurgical silver and various electrodeposits are presented in Table 2. Based on these data, the average values of \( a_0 \) were determined for each kind of silver, and obtained data are shown in Fig. 2.

![Fig. 1. The XRD patterns of metallurgic and electrodeposited silver. The types of electroplating baths are marked above spectra. Formulations and conditions of electrodeposition are presented in “Experimental”](image-url)
The silver deposits obtained from cyanide, DCAT and thiocyanate electroplating baths have a lattice parameter as 4.025 – 4.030 Å that is very close to metallurgic silver if standard deviation was taken into account. In these cases the standard deviation did not exceed 0.035 Å. The electrodeposits obtained from the BPC and sulfite baths have a strained lattice with increased value of $a_0$ up to 4.078 Å (standard deviation 0.003 Å) regardless the predominating of high packing planes (111) and (200). Probably, this difference in $a_0$ values of thin films is caused by different orientation of nucleus at early growth stage dependently on the adsorption energy of ad-atoms [17].

Probably, the differences in $a_0$ values define the different properties of deposits. For example, Ag obtained from the cyanide bath has similar to metallurgic Ag value of $a_0$ and possesses similar to ones a corrosion behavior [19]. Whereas deposits obtained from BPC bath having deformed lattice possess lower corrosion resistance in comparison with metallurgic silver [4].

The calculation of grain size and dimensionless values of microstrain are performed by measuring the broadening of a particular peak in a diffraction pattern associated with a particular planar reflection from within the crystal unit cell. It is inversely related to the FWHM (full width at half maximum-broadening) of an individual peak - the more narrow the peak, the larger the crystallite size. For the grain size calculation the formula given originally by Scherrer:

$$\beta = \frac{K\lambda}{\tau \cos \theta_{hl}} $$

where: $\beta$ is the peak broadening (in rad); $K$ is the Scherrer factor and the digital constant as 0.94 is the best for cubic structure in the expression; $\tau$ is the grain size (in Å).

If this is the only reason for the broadening, then the value $\beta \cos \theta_{hl}$ should be independent of the diffraction angle. However, the real situation is different, because of the persistence of the additional stress-induced broadening $\beta_\varepsilon$ which is given by the Wilson formula:

$$\beta_\varepsilon = 4\varepsilon \tan \theta_{hl} $$

where $\varepsilon$ is a dimensionless value ("microstrain").

The value of $\varepsilon$ is usually assumed to be proportional to the square root of the density of dislocations. Note that "size" and "strain" broadening show different $\theta$ dependence. This provides a way to separate the two dependences. Assuming the shape of the line profiles to be of Gaussian form and both the grain size and microstrain contribute to the line broadening, the integral width, $\beta$, of the structurally broadened profile is given by [18]:

$$\beta^2 = \beta_\tau^2 + \beta_\varepsilon^2 = \left(\frac{K\lambda}{\tau \cos \theta}\right)^2 + (4\varepsilon \tan \theta)^2. $$

### Table 2. Lattice parameter ($a_0$) and interplanar spacing ($d_{hkl}$) for silver obtained by metallurgy and electroplated from various solutions

<table>
<thead>
<tr>
<th></th>
<th>Metallurg. Ag</th>
<th>From cyanide</th>
<th>From DCAT</th>
<th>From BPC</th>
<th>From thiocyanate</th>
<th>From sulfite</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>$\theta$, deg</td>
<td>19.56</td>
<td>19.56</td>
<td>19.81</td>
<td>19.115</td>
<td>19.67</td>
</tr>
<tr>
<td></td>
<td>$d_{hkl}$, Å</td>
<td>2.3008</td>
<td>2.3008</td>
<td>2.2729</td>
<td>2.3522</td>
<td>2.2884</td>
</tr>
<tr>
<td></td>
<td>$a_0$, Å</td>
<td>3.9850</td>
<td>3.9850</td>
<td>3.9367</td>
<td>4.0742</td>
<td>3.9636</td>
</tr>
<tr>
<td>(200)</td>
<td>$\theta$, deg</td>
<td>22.63</td>
<td>22.66</td>
<td>22.90</td>
<td>22.17</td>
<td>22.79</td>
</tr>
<tr>
<td></td>
<td>$d_{hkl}$, Å</td>
<td>2.0023</td>
<td>1.9994</td>
<td>1.9795</td>
<td>2.0413</td>
<td>1.9886</td>
</tr>
<tr>
<td></td>
<td>$a_0$, Å</td>
<td>4.0406</td>
<td>3.9987</td>
<td>3.9590</td>
<td>4.0825</td>
<td>3.9771</td>
</tr>
<tr>
<td>(220)</td>
<td>$\theta$, deg</td>
<td>32.68</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>32.88</td>
</tr>
<tr>
<td></td>
<td>$d_{hkl}$, Å</td>
<td>1.4266</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.4189</td>
</tr>
<tr>
<td></td>
<td>$a_0$, Å</td>
<td>4.0350</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4.0132</td>
</tr>
<tr>
<td>(311)</td>
<td>$\theta$, deg</td>
<td>39.12</td>
<td>39.18</td>
<td>39.41</td>
<td>38.80</td>
<td>39.33</td>
</tr>
<tr>
<td></td>
<td>$d_{hkl}$, Å</td>
<td>1.2208</td>
<td>1.2193</td>
<td>1.2133</td>
<td>1.2293</td>
<td>1.2154</td>
</tr>
<tr>
<td></td>
<td>$a_0$, Å</td>
<td>4.0490</td>
<td>4.0438</td>
<td>4.024</td>
<td>4.0771</td>
<td>4.0309</td>
</tr>
<tr>
<td>(222)</td>
<td>$\theta$, deg</td>
<td>41.16</td>
<td>41.27</td>
<td>41.45</td>
<td>–</td>
<td>41.45</td>
</tr>
<tr>
<td></td>
<td>$d_{hkl}$, Å</td>
<td>1.7103</td>
<td>1.1678</td>
<td>1.1636</td>
<td>–</td>
<td>1.1636</td>
</tr>
<tr>
<td></td>
<td>$a_0$, Å</td>
<td>4.0542</td>
<td>4.0453</td>
<td>4.0309</td>
<td>–</td>
<td>4.0309</td>
</tr>
</tbody>
</table>

Fig. 2. Average values of lattice parameter ($a_0$) and evaluated standard deviation based on the data presented in Table 2

Plotting $\beta^2 \cos^2 \theta/(K\lambda)^2$ against $\sin^2 \theta/\lambda^2$ and extrapolating the line to $\sin^2 \theta/\lambda^2 = 0$ allows the estimation of $K^2/\tau^2$ and the slope of the line yields $16\varepsilon^2$, from which
the grain size $\tau$ and microstrain $\varepsilon$ were calculated. The two characteristic sampling plots are presented in Fig. 3.

![Graph showing the grain size $\tau$ and microstrain $\varepsilon$]

Fig. 3. Dependences for $\tau$ and $\varepsilon$ evaluation (see text above)

As it is seen, for metallurgical silver the mentioned dependence is obtained in accordance with Eq. (5), i.e. linear growth ($\varepsilon = 0.00177$) with argument increasing. In this case, the both two factors (grain size and microstrain) governed a XRD peak broadening. For silver obtained from sulfite baths as well as in other studied cases, the mentioned dependencies are weaker and rather proof a scattered character of values. That could occur in one case, namely, if the XRD peaks broadening is governed just by grain size, whereas an effect of microstrain is negligible. The average values of grain size for metallurgical silver and electrodeposited from various kinds of baths are presented in Table 3. As follows from the presented data, the obtained electrodeposits are nanocrystalline. The smallest grains are obtaining in metallurgical silver, but similar values were found also for silver electrodeposits obtained from DCAT, thiocyanate and sulfite solutions.

<table>
<thead>
<tr>
<th>Ag obtaining method or bath</th>
<th>Grain size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallurgical Ag</td>
<td>35.9</td>
</tr>
<tr>
<td>From cyanide</td>
<td>44.1</td>
</tr>
<tr>
<td>From DCAT</td>
<td>36.9</td>
</tr>
<tr>
<td>From BPC</td>
<td>56.5</td>
</tr>
<tr>
<td>From thiocyanate</td>
<td>39.2</td>
</tr>
<tr>
<td>From sulfite</td>
<td>37.3</td>
</tr>
</tbody>
</table>

Table 3. The average grain sizes for silver obtained by metallurgy and electroplated from various solutions

**STM study.** Morphology is probably the most important property of electrodeposited metals and it governs the applicability of each coating. The STM images of electrodeposits obtained from various baths are shown in Fig. 4. As it can be seen, excluding deposits obtained from the BPC baths, the surface of other deposits is less or more uniform and consists of homogeneously distributed grains. The surface of deposits obtained from BPC bath consists of coalesced grains with small fibers of 3 – 10 nm in length.

The roughness ($R_a$) was chosen as a quantitative parameter characterizing the morphology of surface, which is determined as arithmetic average of the absolute values of the surface height deviations measured from the mean plane.

![ STM study images of silver deposits obtained from various baths]

Fig. 4. Characteristic 3-D STM images of silver deposits obtained from various baths: a – from cyanide, b – from DCAT, c – from BPC, d – from sulfite. Formulations and conditions of electrodeposition are noted in “Experimental”
Table 4. The average roughness of substrate (polished brass) and silver deposits obtained by metallurgy and electroplating from various solutions (10 µm × 10 µm area scan)

<table>
<thead>
<tr>
<th>Surface</th>
<th>Average roughness, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate (polished brass)</td>
<td>4.5</td>
</tr>
<tr>
<td>From cyanide</td>
<td>39.5</td>
</tr>
<tr>
<td>From DCAT</td>
<td>34.3</td>
</tr>
<tr>
<td>From BPC</td>
<td>80.8</td>
</tr>
<tr>
<td>From thiocyanate</td>
<td>44.6</td>
</tr>
<tr>
<td>From sulfite</td>
<td>56.4</td>
</tr>
</tbody>
</table>

The values of average roughness obtained on the area scanned 10 µm × 10 µm for polished brass substrate and silver deposits are presented in Table 4. As it is seen, the minimal roughness is observed for the deposits obtained from cyanide and DCAT baths, and the highest was found for deposits obtained from BPC baths. It should be noted that the values of roughness well-correlate with lattice parameter of deposits: the less $a$ the less roughness.

4. CONCLUSIONS

1. Structural analysis of phases and other structural parameters of electroplated silver deposits were done based on the XRD patterns. The deposits obtained from the thiocyanate or sulfite baths contain all possible textures like of metallurgical silver, whereas deposits obtained from the cyanide, DCAT and BPC baths do not contain texture (220) or relevant peak is negligibly low. Moreover, the textures (311) and (222) almost are absent in deposits, obtained from the BPC bath.

2. The silver deposits obtained from cyanide, DCAT and thiocyanate electroplating baths have a lattice parameter and interplanar distance very close to metallurgical silver if standard deviation would be taken into account.

3. The obtained electrodeposits are nanocrystalline. The smallest grains are obtained in metallurgical silver, but similar values were found also for silver electrodeposits obtained from DCAT, thiocyanate and sulfite baths.

4. The minimal roughness (34 – 39 nm) is observed for the deposits obtained from cyanide and DCAT baths and highest as 81 nm was found for deposits obtained from BPC baths.

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