Impact of post annealing on the electrical properties of silver nanofilms

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Abstract This paper reports on the growth of nanostructures of silver films prepared by thermal evaporation in vacuum. We focused on the effect of annealing on the silver films’ electrical properties. The resistance of the sample was measured by the standard four-probe technique. The electrical resistivity data pertaining to the impact of annealing was analyzed with the help of Fuchs-Sondheimer (F-S) and Mayadas-Shatzkes (M-S) theories.

Keywords: Electrical resistivity, Annealing, Fuchs-Sondheimer (F-S), Mayadas-Shatzkes (M-S) theories.

1. Introduction
Silver has long been utilized for coating mirrors and table ware due to its high light reflecting power. In special cases, silver island films or small particles have been applied as photographic materials, tools and devices to generate localized electric fields or for molecular detection and electric field enhancement [1]. Silver has high electrical and thermal conductivity in bulk form. The electrical properties of the silver films can be improved by altering the film deposition parameters along with the thickness. Therefore, here we address the impact of annealing on the electrical properties of silver films.

2. Experimental Section
Silver nanofilms were fabricated by thermal evaporation in vacuum. The separation between the substrate and the evaporation source was around 0.22 m. The rate of deposition was 0.2 nm/s. Silver of 99.99% purity, Leico Industries, New York, USA, was evaporated onto glass substrates held at room temperature (22 °C). Prior to deposition, the glass substrates were subjected to a series of cleaning processes, such as using detergent and chromic acid, ultrasonic rinsing in distilled water, baking and finally, ionic bombardment in a vacuum chamber. Silver pieces were placed in a molybdenum boat and heated by a strong electric current. Due to Joule heating, the boat becomes red hot and the silver material evaporation begins. The evaporated silver atoms travel along a straight line in vacuum and condensation of these atoms takes place on the substrate kept above the evaporation source. This gives rise to the formation of silver films. The silver films’ resistance was measured by the standard four-
probe method. The films’ thickness was determined using a digital quartz-crystal thickness monitor housed in the vacuum chamber above the evaporation source.

3. Theoretical Section

Electrical conduction in bulk metals arises from the valence electrons of the constituent atoms. Metallic substances have high thermal and electrical conductivities because of the presence of a large number of free electrons. This was first proposed by Drude [2] in 1900 and later verified by Lorentz [3] in 1904-05. According to Mathiessen’s rule [4], the total electrical resistivity [5] of a bulk sample, \( \rho_B \), is equivalent to the sum of resistivities arising from different scattering processes (Maissel, 1970) [5] i.e.,

\[
\rho_B = \rho_T + \rho_V + \rho_I
\]  
(1)

where \( \rho_T \) is the component of the resistivity due to the thermal vibrations of the lattice atoms, \( \rho_V \) is due to vacancies and \( \rho_I \) is due to impurities. An accurate study of the size effect was conducted by F-S by solving Bolzmann’s transport equation [6] with appropriate boundary conditions. They derived an expression for the resistivity, \( \rho \), [7]

\[
\rho = \rho_0 [1 + \frac{3}{8 \lambda} (1 - p)], \lambda > 0.1
\]
(2)

where \( \rho_0 \) is the resistivity of an infinitely thick film, \( l \) is the conduction electrons mean free path, \( t \) is the thickness of the film. Equation (2) works well over a wide range of \( \lambda = \frac{t}{l} \). Further, this expression applies to completely diffuse reflection, whereby the conduction electrons lose their energy in the field direction after collisions with the film surfaces. F-S introduced a pecularity parameter, \( p \), representing the part of electrons that are specularly scattered from the film surfaces, so that the electrons contribute to the conductivity even after being scattered off the surfaces. The pecularity parameter, \( p \), is a dimensionless quantity having values in the range from 0 to 1, the extremities being a totally diffuse (0) and a totally specular (1) scattering. According to F-S, \( p \) is an empirical constant. What causes the diffuse scattering [24] is not yet known; it may be due to the angle at which the carriers are incident on the surface of the film causing scattering and the frequency of collisions. Thus, the total film resistivity can be derived [8-11]. The first term in the Eqn (2) represents the background resistivity, while the second term indicates the resistivity due to the size effect. The F-S theory explains the experimental results of resistivity only for films of larger thicknesses. However, a discrepancy arises between the experimental and the F-S theoretical resistivity data for lower film thicknesses. M-S [12] modified the F-S resistivity equation by incorporating grain boundary scattering, which may be written as

\[
\rho = \rho_0 [1 + \frac{3}{8 \lambda} (1 - p) + \frac{3}{2} \alpha' + \ldots \ldots],
\]  
(3)

where \( \alpha' \) is the grains boundaries scattering power. M-S assumed a grain size nearly equal to the film thickness up to a certain limit. After this limit, \( l \) becomes too small in comparison with the size of the grain boundaries, leading to zero contribution to the total resistivity.

4. Results and Discussion

We annealed the silver films in-situ at a temperature of 100 °C for two hours. There was an appreciable change in the resistance upon annealing along with the other parameters as shown in
Figure 1, which displays the F-S and M-S theoretical results and our experimental curves for both non-annealed and annealed silver films.

![Graph showing resistivity vs thickness for silver films](image)

**Figure 1.** Resistivity ($\rho$) versus thickness ($t$) of silver films.

**Supplementary Data: Figure 1.**

| Thickness ($t$) in nm | Non-annealed ($\rho_{\text{Fuchs}}$) $\times 10^8$ $\Omega$ m | Non-annealed ($\rho_{\text{exp}}$) $\times 10^8$ $\Omega$ m | Annealed ($\rho_{\text{Fuchs}}$) $\times 10^8$ $\Omega$ m | Annealed ($\rho_{\text{exp}}$) $\times 10^8$ $\Omega$ m |
|----------------------|-------------------------------------------------|-------------------------------------------------|---------------------------------|---------------------|
| 50                   | 4.665                                           | 5.826                                           | 2.58                            | 3.74                |
| 60                   | 4.476                                           | 5.024                                           | 2.542                           | 3.00                |
| 70                   | 4.341                                           | 4.54                                            | 2.517                           | 2.70                |
| 80                   | 4.24                                            | 4.24                                            | 2.55                            | 2.55                |
| 90                   | 4.161                                           | 4.161                                           | 2.45                            | 2.45                |
| 110                  | 4.047                                           | 4.047                                           | 2.45                            | 2.45                |
| 130                  | 3.967                                           | 3.967                                           | 2.45                            | 2.45                |
| 150                  | 3.909                                           | 3.909                                           | 2.45                            | 2.45                |

Figure 2 is a plot of ($\rho \times t$) vs ($t$) for both non-annealed and annealed silver films. The various parameters estimated from the slopes and intercepts of the two straight lines are listed in Table 1.
Figure 2. Resistivity ($\rho \times t$) versus thickness ($t$) for silver films, $t > 80$ nm.

Supplementary Data: Figure 2.

| Thickness ($t$) in nm | Un-annealed $\times 10^{-8}$ $\Omega$ m | Annealed $\times 10^{-8}$ $\Omega$ m |
|-----------------------|----------------------------------------|---------------------------------------|
| 80                    | 339.22                                 | 204                                   |
| 90                    | 374.53                                 | 220.5                                 |
| 110                   | 445.17                                 | 269.5                                 |
| 130                   | 515.80                                 | 318.5                                 |
| 150                   | 586.44                                 | 367.5                                 |

Table 1. Annealing-based electrical parameters of silver films

| Material             | Thermal position | $\rho_0$ ($\times 10^3$) $\Omega$ m | $l(1-p)$ nm | $l$ (nm) | $p$   |
|----------------------|------------------|------------------------------------|-------------|----------|-------|
| Silver Non-annealed  |                  | 3.539                              | 42.8        | 42.8     | 0     |
|                      | film             |                                    |             |          |       |
| Silver Annealed Ag   |                  | 2.37                               | 11.634      | 14.54    | 0.2   |
| film at 100°C        |                  |                                    |             |          |       |

Films deposited by evaporation usually harbor a large number of defects, unless great care is taken to avoid them. It is possible to remove these defects by annealing, which generally results in a decrease in the film resistivity [13]. A reduction upon annealing of 20-50% of the resistance of 24 elements has
been reported by Belser [14]. We found that annealing at 100 °C at a pressure of 10⁶ Torr lowered the annealed film’s resistivity about 1.5 times compared with that of the non-annealed film.

5. Conclusions
The resistance of a metal film decreases rapidly on annealing as observed in the cases of silver and other metallic films. The F-S theory fits well our experimental resistivity versus thickness data for thicknesses greater than 80 nm. The F-S theory does not consider the grain boundary scattering mechanism, which is predominant in very thin films. The M-S theory explains our experimental results faithfully for annealed and non-annealed films. The annealing improves the electrical characteristics of silver films.

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