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Impact of substrate temperature on surface and grain boundary reflection in thin chromium nanofilms

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Abstract. The impact of substrate temperature on surface and grain boundary reflection is studied as a function of thickness of chromium nanofilms in the range, 10-80 nm. Substrate temperature happens to be one of the important and crucial deposition parameters, which regulates many physical properties of evaporated thin films. Hence, we have deposited the chromium nanofilms at four different substrate temperatures (Ts = 22, 100, 150 & 1800C) in order to study and analyze its effect on surface and grain boundary reflections and other electrical properties. In this work a qualitative analysis of both surface and grain boundary reflections of thin chromium nanofilms with independent variation of thickness is reported. The grain boundary reflection coefficients (R) have been calculated by estimating the resistivity data of the chromium nanofilms using Mayadas-Shatzkes and Fuchs-Sondheimer models. The substrate temperature dependent resistivity of chromium films exhibit an unusual behavior.

1. Introduction
Thin chromium films have found many applications for example it was the first metal to be investigated as a thin film resistor material, and is used in photo-masks, integrated circuits, optical beam splitters, semi-reflection coating and the magnetic recording disks. Other applications exist such as thin film capacitor plates and antimagnetic shielding materials [1].

In the present article, the impact of substrate temperature (Ts) on the electrical resistivity, surface and grain boundary reflections of chromium nanofilms is explored in the thickness range 10-80 nm. The thin nanofilms of chromium have been grown by thermal evaporation in vacuum onto glass substrates as it is capable of yielding good quality thin films. The majority of physical properties of thin films utilized for practical applications depend, to a great extent, on thickness as well deposition parameters. The deposition conditions include substrate temperature [2-5], substrate materials [6-8], deposition pressure [9], deposition rate [10], application of DC field [11, 12] during the formation of the film, etc. play a vital role in the nucleation, growth and other characteristics of nano-films. Tailoring of deposition parameters is the main topical issue for their application in electronics. The goal of the present work is
the investigation of the impact of substrate temperature on the electrical properties including surface and grain boundary reflection of chromium nano-metric films deposited by resistive heating method in vacuum, onto glass substrates, because of their smooth surface and dielectric nature. The reason for selecting this thickness range, 10-80 nm, is that we have first estimated the conduction electron mean free path in bulk chromium [13] from its resistivity data, which is around 15.2 nm. The microstructure of chromium films have been investigated from AFM & SEM images. Initial EDS analysis usually involves the generation of an X-ray spectrum from the entire scan area of the material under investigation and the material is identified as chromium.

2. Theoretical section
The electrical resistivity of thin films, based on the Fuchs-Sondheimer(FS) theory [14,15] is given by

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

where \( \rho \) = resistivity of thin film, 
\( \rho_0 \) = the resistivity of the infinitely thick film, 
\( \lambda \) = the ratio of the film thickness(t), to the conduction electron mean free path (l),
\( p \) = the specularity parameter.

The second term on the Right Hand Side (RHS) of Eqn. (1) is the contribution to the electrical resistivity from size effect. Taking into account of grain boundary scattering, which is predominant in very thin films, Mayadas - Shatzkes modified the above equation as [16]

\[ \rho = \rho_0 \left[ 1 + \frac{3}{8} \left(1 - \frac{p}{\lambda}\right) \lambda + \frac{3}{2} \alpha' + \ldots \right] \quad \text{...............(2)} \]

where \( \alpha' = l(R) / d(1 - R) \) = the scattering power of grain boundaries which depends upon the electron mean free path(l) and average grain size(d) and R being the grain boundary reflection coefficient. The third term on the RHS of Eqn. (2) is contribution to the electrical resistivity from grain boundary scattering.

3. Experimental Section
Chromium nano-thin films have been successfully deposited onto soda lime glass. The experimental method of preparation are given elsewhere [17,18]. The electrical resistivity measurements have been performed, in-situ, carefully, by the standard four point probe technique[19].

4. Results and Discussions
Figure 1 shows the graph of electrical resistivity (\( \rho \)) versus nano film thickness (t) for chromium films grown on glass substrates at different substrate temperature (T_s = 22, 100, 150 & 180°C). It is evident from the same figure that the electrical resistivity is quite large for lower thickness films and decreases for higher thicknesses, and finally attains a constant values of about 51, 95, 140 and 72 \( \times 10^8 \Omega \text{m} \), respectively after a thickness of 40 nm.
Figure 1. Plot of Electrical Resistivity($\rho$) against chromium nano-film thickness($t$) grown at different $T_S$. (= 22, 100, 150 & 180°C), based upon F-S theory and our experimental results.

Figure 2 shows ($\rho \times t$) vs $t$ graphs, which have been plotted for chromium nano-films deposited simultaneously, onto glass substrates at different substrate temperatures (22, 100, 150 & 180°C).

The slopes of these graphs, according to Eqn.(2), give $\rho_0$, the infinitely thick film resistivity, as 49.6, 85.9, 126, and $63.1 \times 10^8$ $\Omega$ m, respectively for the films deposited at $T_S$ = 22, 100, 150 and 180°C, and the intercepts on the ($\rho \times t$) axis give $3 \rho_0/(1-p)/8$, as 260 and 492, 712, and $424 \times 10^{-17}$ $\Omega$m$^2$. We tried to fit our experimental data on the basis of FS theory by assigning different values for $p$; the best fit is obtained for $p = 0.1, 0.2, 0.15$ and $0.25$ respectively for the films grown at different substrate temperatures and these values are given in Table 1. The resistivity $\rho_0$ (12.9, 85.9 & 63.1 $\times 10^8$ $\Omega$ m) of an infinitely thick chromium nano-film, grown at different $T_S$, estimated from the Fig. 2 are quite high in comparison with the bulk resistivity of chromium [20].
Figure 2. Plot of \((\rho \times t)\) versus \((t)\) for chromium nanofilms grown at different \(T_s\) (= 22, 100, 150 & 180\(^0\)C) for the thicknesses > 30 nm.

Table 1. (for Chromium nanofilms)

| Sl. No. | Parameter | Substrate Temperature(\(T_s\)) |
|---------|-----------|-------------------------------|
|         |           | 22\(^0\) C | 100\(^0\) C | 150\(^0\) C | 180\(^0\) C |
|         | \((t)\) in nm | \(R_1 \times 10^3\) | \(R_2 \times 10^3\) | \(R_3 \times 10^3\) | \(R_4 \times 10^3\) |
| 1       | 10        | 25          | 15.3       | 7.4         | 23          |
| 2       | 15        | 33          | 18         | 12.1        | 30          |
| 3       | 20        | 34          | 12         | 16          | 24          |
| 4       | 30        | 15.6        | 12         | 20          | 24          |
| 5       | \((R_\text{average})\) | 26.9        | 14.32      | 9.3         | 25.3        |

| Parameter | Substrate Temperature(\(T_s\)) |
|-----------|-------------------------------|
|           | 22\(^0\) C | 100\(^0\) C | 150\(^0\) C | 180\(^0\) C |
| 6 \(\rho_0\) | 49.6 \times 10^{-8} \Omega m | 85.9 \times 10^{-8} \Omega m | 126 \times 10^{-8} \Omega m | 63.1 \times 10^{-8} \Omega m |
| 7 \((l-p)\) | 14 nm | 16 nm | 15.1 nm | 18 nm |
| 8 \(l\) | 15.3 nm | 20 nm | 17.8 nm | 24 nm |
| 9 \(p\) | 0.1 | 0.2 | 0.5 | 0.25 |

The curves based on FS theory are shown in Fig. 1 by the lower curves, for the chromium films deposited at \((T_s,= 22, 100, 150 & 180\(^0\)C)\), while the upper ones represent the experimental curves.
We obtained good agreement between FS theory and experimental data for higher thicknesses $> 30$ nm for all the films grown at different substrate temperatures. Making use of the values $\rho_0$ and $p$, values of $l$ have been calculated for the films grown at different substrate temperatures which are given in Table I. 

Even though there is perfect agreement between F-S theoretical and our experimental curves for higher thickness films, there is, however, some deviation from the theoretical curves for lower thickness films. This is attributed to the fact that the F-S theory takes into account the variation due to size effect and disregards the grain boundary scattering, which is predominant in lower thickness films. Similar deviation at lower thicknesses between FS theory and experimental data has also been reported for palladium [21], samarium [22], manganese [23], yttrium [24], ytterbium [25] and tin [26] films.

We tried to fit our experimental data with MS theory. The theoretical curves based on MS theory are denoted by the upper curves in Figure 1, for chromium films grown at different $T_S$. It is clear from the Figure 1 that there is good agreement between the MS theory and the experimental data for thinner films where grain boundary scattering is predominant. To calculate the grain boundary reflection coefficient ($R$), we assumed the grain diameter to be equal to the thickness of the film, i.e., up to 30 nm for glass at different $T_S$, below which the experimental data deviate from the FS theoretical curves. However, for higher thicknesses ($> 30$ nm) the grain diameter becomes very large in comparison with the mean free path of the conduction electron and hence contribution to the film resistivity from the grain boundaries become negligible.

The difference between the resistivity from the F-S theoretical curve and the experimental data gives $\left(3\alpha'\rho_0/2\right)$. Using the values of $\rho_0$ and $l$ estimated from the Fuchs theory, we obtained the value of $\alpha'$ and from this the constant $R_{av}$ ($R$ average) are found to be 26.9, 14.32, 9.3 and $25.3 \times 10^{-3}$, respectively, for the films grown at different substrate temperatures, 22, 100, 150 and $180^\circ$ C, which are mentioned in the Table I. These are used in the equation (2) to obtain MS theoretical curve.

Figure 3 shows the variation of grain boundary reflection coefficient ($R$) with substrate temperature ($T_S$) for chromium nanofilms.
The growth and structure of evaporated films are very much affected by the nature of the substrates, smoothness/roughness and the binding force between them (substrates), evaporated atoms and substrate temperature. An increase in the binding force between the substrate and evaporated atoms usually decreases the surface mobility of evaporated atoms and hence increases the population of critical nuclei. This in turn enhances the film adhesion. Therefore, the film resistivity may be reduced considerably.

The theoretical curves based on the M-S theory are shown in Fig. 1. It is clear from this figure, that there is good agreement between M-S theory and our experimental data for chromium films coated at different Ts, for thinner films where grain boundary scattering is predominant. The average grain boundary reflection coefficient, $R_{ab}$, as mentioned in the Table I for Cr coated at substrate temperatures 22, 100 & 150°C appears to decrease with the increase in Ts up to 150°C and then afterwards it increases at Ts=180°C. The conduction electron mean free path ($l$), infinitely thick film resistivity ($\rho_0$) and specularity parameter($p$) also follows the same path or order in respect of Ts. However, the grain boundary reflection coefficient varies with Ts, in the reverse order, that is with an increase in Ts, the grain boundary reflection coefficient first decreases up to Ts = 150°C and then after words R increases as shown in Table I and Fig. 3. Similar results have been reported for Ni-Si silicide films [27]. It is reported that ($\rho_0$) and ($l$) are different and dependent on Ts for Antimony [28].film. The variation in the reflection coefficient with Ts may be due to the enrichment of impurities in the grain boundaries[29].

5. Conclusion
It is found that the Fuchs-Sondheimer theory considers only the size effect avoiding the grain boundary scattering. The grain boundary scattering mechanism is predominant in thin nanofilms below the thickness of the electron mean free path which has been taken into account by Mayadas - Shatzkes. Our experimental curves fit well with Mayadas – Shatzkes theoretical curves.
We have calculated the values of $\rho_0$, $\rho$, $p$ and $l$ for chromium films grown at different $T_s$. By tuning the grain size during the film formation, we discriminate whether the dominant collision mechanism controlling the resistivity of nanofilms is electron-surface or electron-grain boundary scattering.

With the use of the electron conduction model proposed by Mayadas-Shatzkes, we have calculated the fraction ($p$) of electrons which are specularly reflected at the surface of the film and the grain boundary reflection coefficient ($R$), at different $T_s$. We have also deduced the electron mean free path from these results.

We found that the factors correlated to the electrical resistivity of the nano-films also govern the grain size and grain boundary reflection.

The grain boundary theory of Mayadas-Shatzkes reproduces our experimental observations faithfully even at different $T_s$. The grain boundary reflection plays a significant role in electron transport mechanism in chromium nanofilms [30].

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