VARIATION IN REFRACTIVE INDEX AND EXTINCTION COEFFICIENT OF A VERY THIN COPPER FILM BY THERMAL ANNEALING: AN ELLIPSOMETRIC APPROACH**

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A pure experiment-based work was conducted to investigate the optical characteristics of a thin absorbing single-layer copper film at various annealing temperatures. The study also systematically examined the utilization of spectroscopic ellipsometry as an effective tool for fine-tuning the optical constants of thin films, particularly for achieving specific refractive index (n) and extinction coefficient (k) values. The measurement and analysis involved a thermally deposited thin nano-sized single-layer copper film on a glass substrate, along with a spectroscopic ellipsometer.

Keywords: *copper, metallic film, glass substrate, spectroscopic ellipsometry.*

ЭЛЛИПСОМЕТРИЧЕСКИЙ ПОДХОД В ИЗУЧЕНИИ ИЗМЕНЕНИЙ ПОКАЗАТЕЛЯ ПРЕЛОМЛЕНИЯ И КОЭФФИЦИЕНТА ЭКСТИНКЦИИ ТОНКОЙ ОДНОСЛОЙНОЙ ПЛЕНКИ МЕДИ ПРИ ТЕРМИЧЕСКОМ ОТЖИГЕ

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Исследованы оптические характеристики тонкой поглощающей однослойной пленки меди при различных температурах отжига. Спектроскопическая эллипсометрия применена в качестве эффективного инструмента для точной настройки оптических констант тонких пленок, особенно для достижения конкретных значений показателя преломления (n) и коэффициента экстинкции (k). Измерение и анализ термически осажденной на стеклянную подложку тонкой однослойной пленки меди проведены для спектроскопического эллипсометра.

Ключевые слова: *медь, металлическая пленка, стеклянная подложка, спектроскопическая эллипсометрия.*

Introduction. Copper (Cu) is considered one of the most practically suitable materials for making single-layer films for various electronic and optical applications. Thin copper films are very common in electronic devices due to their applications, such as neutral density filters, thin conducting electrodes, antireflection surfaces, microstrip antennas, heat sinks, etc. [1–3]. In many electronic devices, these films are typically deposited on substrates such as glass, quartz, or flexible free-standing polymer films. Sometimes different application-specific patterns for small MEMS circuits can also be designed by etching processes on these films [4]. Copper nanofilms with a high refractive index and low extinction coefficient can be used as transparent conductive electrodes in optoelectronic devices such as solar cells and touch screens [5–7]. The refractive index is a measure of how much light bends as it passes through a material, and the extinction coefficient is a measure of how much of the light is absorbed by the material. Both parameters are related to

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the electronic and optical properties of the material, including the plasmonic properties of the copper nanofilm. Copper nanofilms with tunable refractive index (n) and extinction coefficient (k) can be used as optical filters for selective wavelength filtering and colour tuning [8–10]. Generally, a film with high refractive index can enhance the light-trapping properties of the device, while a low extinction coefficient can reduce light absorption and increase transmission [11]. By controlling the thickness and pattern of the copper nanofilm, it is possible to create filters with specific transmission or reflection spectra [12]. For these, knowing the properties of thin films on various substrates is very important; spectroscopic ellipsometry is one of such very useful and effective characterization tools for analyzing homogenous thin films on various types of substrates. It is a widely accepted non-destructive optical characterization tool for metallic and polymeric thin films on a dielectric substrate with nanometer thickness [13, 14]. So far various groups have conducted ellipsometric measurements of copper thin films [6, 15]. However, many of those studies are not well focused on the thickness of the films and it is an important parameter for making optical filters based on copper. So, the present work will investigate how the optical constants like the refractive index (n) and extinction coefficient (k) of a nano-sized (<100 nm) copper thin film on a glass substrate vary with thermal annealing conditions using the ellipsometric technique for the application in optical filters.

Experimental. Granules of pure copper metal sourced from Sigma Aldrich were thermally evaporated and deposited on a laboratory-grade glass slide using a “Hind High Vacuum 12A4D” model thermal evaporating machine. A molybdenum-based boat was used for the evaporation and a pretty clean common laboratory-grade transparent glass slide was chosen as a substrate (Cauchy substrate). After deposition, four small films were uniformly cut from a single large unannealed copper thin film on a glass substrate to ensure the uniqueness of the experiment. One film is kept as such for the reference sample at ambient temperature, while the remaining films were annealed in a hot air oven at various temperatures like 200, 300, and 400°C, respectively. Initially, the film appeared as a thin shiny metal film on a Cauchy substrate in nanometer thickness and after annealing, it was transformed into a less reflective oxide film on a Cauchy substrate. Subsequently, the prepared films are characterized under a variable angle M-2000 model spectroscopic ellipsometer from J. A. Woollam Co.

A spectroscopic ellipsometer is an instrument, used to study the interaction of a light beam with a sample by measuring its change in polarization. The M-2000 model variable angle spectroscopic ellipsometer instrument mainly consists of a source, detector, polarization state generator (PSG), and polarization state analyzer (PZA). The source and detector are mounted opposite each other on the two arms of the instrument. The angle of both arms of the instrument can be changed by the program according to Brewster’s angle of the sample material for optimum sensitivity. The source continuously produces a light beam with a range of wavelengths and the detector measures the reflected light from different layers of the film including the substrate. The M-2000 equipment used for the measurement has a quartz tungsten halogen (QTH) lamp as a source with a wavelength range from 370 nm (ultraviolet) to 1000 nm (near-infrared) and a fast CCD detector for data collection. The machine was calibrated with a standard silicon wafer before the actual measurements. The films were scanned at various angles 55, 60, and 65° with an interval of 5°. At least five sample measurements were taken from different parts of the prepared samples. The whole measurement process, like data collection, fitting, and analysis were carried out with the help of the “Complete EASE” software installed in the system. The optical models used for fitting the experimental data were sourced from the library of “Complete EASE” software. For this experiment, two different models were chosen: “7059_cauchy” and the “B-Spline”. The model “7059_Cauchy” is well suited for transparent glass substrates and B-Spline (Basis spline) is a very good model for thin absorbing metallic films. The B-spline and Cauchy models for the thin absorbing films were well described in the publications [16, 17].

Results and discussion. The initial measurement revealed that without any annealing processes, the thin copper film has a thickness of around 45.28 nm (at ambient temperature). The graph in Fig. 1 shows that as the annealing temperature increases the thickness of the film also increased. For the films annealed at 200, 300, and 400°C, the thickness increased to 57.16, 74.15, and 86.56 nm, respectively. This increase in thickness can be attributed to the formation of an oxide layer on the film's surface during annealing. Due to the high temperature, the thin layer of copper metal on the glass slide initially oxidized to cuprous oxide (Cu_2O), which further transformed into cupric oxide (CuO) with additional annealing. According to some previous publications, as the temperature increased from ambient temperature to nearly 150°C, the copper film slowly began to change to Cu_2O and at nearly 280°C, Cu_2O started to change to CuO, while at 400°C, the sample completely transformed into cupric oxide (CuO) [18, 19]. As the oxide layer on the film’s surface increased, the physical thickness of the film also increased. Surface roughness and backside reflection are the other two crucial parameters considered during these measurements. Excessive surface roughness and backside reflection can make ellipsometric characterization and fitting more challenging, leading to the loss of reflected light from the sample to the detector and the loss of some sample data [20]. The experimental data in Table 1 shows that, in annealed films, surface roughness of the film also increased due to oxide deposition on the surface. At 200°C, surface roughness was 18.69±0.156 nm which increased to 32.11±0.065 nm when the film was annealed at 400°C.

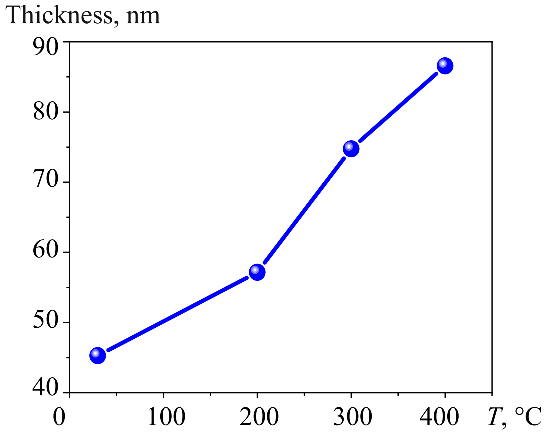

Fig. 1. Thickness versus temperature graph of the copper thin film (room temperature taken as 30°C).

During the annealing process, the microstructure and crystallographic orientation of the copper nanofilm can be changed, leading to changes in its electronic and optical properties. These changes can also affect the refractive index and extinction coefficient of the film, which in turn can affect the propagation and absorption of light through the film [15, 21]. When incident radiation passes through a sample, some portion of it will always attenuate, whereby this change in refractive index can be conveniently defined as a complex refractive index

$n^* = n + ik$ [\displaystyle\underline(n)], (1)

where the real part n is the refractive index and which represents the phase velocity, while the imaginary part k is called the extinction coefficient. Figure 2a shows the fitted data of the refractive index of each film varying with wavelength, as per the data, unannealed copper film has a very low refractive index value, which varies in the value ranging from $n = 0.5$ to 1.5 with respect to wavelength. On the other hand, the annealed or oxidized film has a much higher refractive index compared to the unannealed film, varying between $n = 2$ to 3. Thus, we took the standard wavelength of 632.4 nm for the comparison of the refractive index. According to the fitted results in the Table 1, the refractive index at the standard wavelength increases with the annealing temperature. The refractive index versus the temperature graph in Fig. 3 initially shows that at room temperature film had a very low refractive index ($n = 0.85$) that gradually increased to $n = 2.3$ at 200°C and then slowly increased to $n = 2.7$ at 400 °C. Thus, we can easily control the refractive index of a film using a gradual increase in temperature and simultaneous measurement of the refractive index using an ellipsometer.

The extinction coefficient k is another important parameter mentioned in Eq. (1). It is a measure of how much incident radiation is lost due to scattering and absorption per unit volume of the sample. This means that for high values of extinction coefficient (k), it is in a higher wavelength range, indicating that these films

TABLE 1. Tabulated Results Obtained from Fittings

Sample	Cu (Room temp)	Cu (200°C)	Cu (300°C)	Cu (400°C)	Result
Thickness, nm	45.28	57.16	74.75	86.56	Increased
Refractive index, n	0.85572	2.342	2.49468	2.70964	Increased
Extinction coefficient, k	2.42088	0.659	0.67168	0.31899	Decreased
Mean separation error (MSE)	5.058	3.382	2.21	2.477	Good fit
Roughness, nm	–	18.69 ± 0.156	–	32.11 ± 0.065	Increased

are opaque for that range, whereas a lower *k* value for a lower wavelength range means that the films are not so opaque in that range [22]. In Figure 2b we can see that the same theory happened for the unannealed copper film at 400 to 600 nm, whereby films are comparatively less opaque than the range 600 to 1000 nm. This means that for an unannealed pure metal film, a wide range of wavelengths of the incident radiation is blocked or absorbed by the opaque copper metal film. In the case of annealed film, just the reverse is happening, which means the lower wavelength region from 400 to 600 nm is more opaque than the higher wavelength region from 600–1000 nm. However, the overall *k* value is very small when compared with the *k* value of the unannealed film, which means that the oxide films of copper have much better IR transmittance properties than the unannealed pure copper metal film [2]. Thus, the copper oxide films less than 100 nm thick show much better transparency of incident radiation than the pure copper metal film. For comparison, similar to the standard refractive index, a standard *k* value for different annealed films at 632.4 nm was also plotted in Fig. 3.

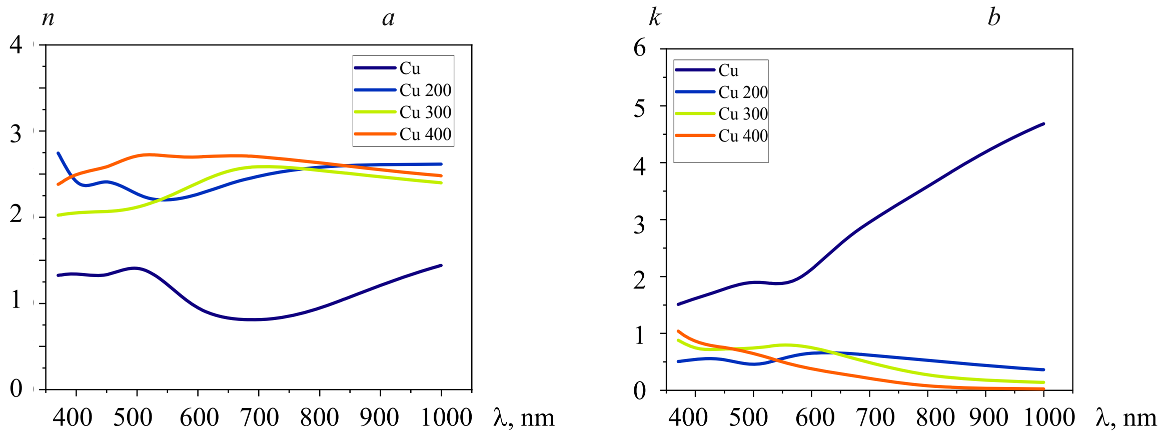

Fig. 2. Change in (a) refractive index *n* and (b) extinction coefficient *k* versus wavelength for copper films annealed at different temperatures.

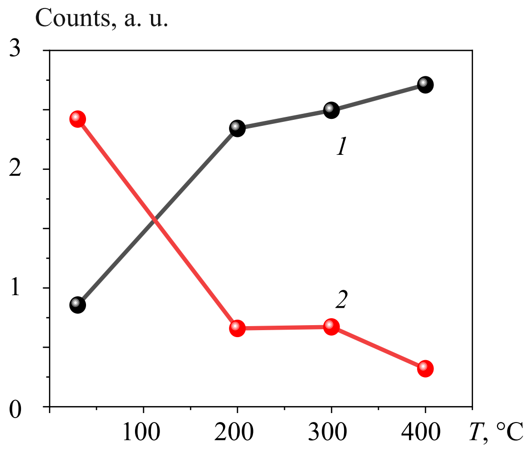

Fig. 3. Change in values of refractive index *n* (1) and extinction coefficient *k* (2) versus temperature at a standard reference wavelength of 632.4 nm.

Analyzing the graph in Fig. 3 we can easily understand that an unannealed film has a maximum *k* value ($k = 2.4$) and when the sample is heated to 200°C, the *k* value suddenly drops to $k = 0.6$, decreasing with the increase in temperature. This means that by annealing a copper metal film, its transparency to the incident radiation increases with temperature [23]. The very low MSE (mean separation error) value of less than five, obtained during each fitting also supports the quality of the data received.

Conclusions. A very thin layer of copper film was successfully vacuum deposited on a glass substrate and its optical behaviours were studied with an increase in temperature using spectroscopic ellipsometry. The obtained results suggest that, through precise annealing and fast ellipsometric measurements, we can control the properties of thin copper films with specific n and k values for various optical and electronic applications. The obtained results also suggest the potential application of copper films (<100 nm) for the preparation of optical filters with a high refractive index and low extinction coefficient.

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