Thickness optimization of ultrathin nickel films as transparent conductive electrodes

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(Dated: **15 December 2017**)

Ultrathin nickel films with thicknesses varying from 2-7 nm in 1 nm increments were produced using electron-beam physical vapor deposition. Optical transmittance spectra were obtained using ellipsometry and Fourier transform infrared spectroscopy, and resistivities were obtained by measuring sheet resistance using a four-point probe setup. The Haacke's figure of merit was used to determine the optimal thickness of 3 nm for those films produced, and a relative slope method was used along with fits to obtained data to determine a more precise optimum of 3.3 nm. Differences in transmittance and resistivity from other sources were attributed to the lesser degree of compacting in the deposition method used when compared to dc sputtering. The results show that nickel thin films can be optimized by thickness to produce transparent conductive electrodes for optoelectronic applications.

PACS numbers: 81.05.Bx, 81.15.Dj, 81.70.Ex, 81.70.Fy
Keywords: metallic thin films, nickel, electrical conductivity, transparency, infrared spectra, visible spectra, electron beam deposition

I. INTRODUCTION

There is interest in the development of ultrathin metal films for optoelectronic applications, with their potential for use as transparent conductive electrodes. Such films find use in devices such as organic solar cells and light emitting diodes, where a film electrode contact is required to protect the moisture-sensitive materials within. In addition to having good conductivity to be useful as contacts, these films must naturally be transparent to the light such devices interact with in order to keep efficiency high. Currently, the most popular film material is indium tin oxide (ITO), a ceramic oxide. This material has several drawbacks that limit its applicability, including poor stability, inflexibility, fragility, and poor transmission in the ultraviolet (UV) and infrared (IR) wavelength ranges[1]. Ultrathin metal films have the potential to overcome these drawbacks and perform better than ITO in relevant applications[2]. Nickel is chosen as the film material of choice for this study for its relative stability and transparency compared to other metals[3].

Some potential drawbacks of metal films that must first be addressed are film stability, the decrease in resistivity compared to bulk material, and the high absorption associated with metals. The attenuation of light as it travels through a metal is described by the imaginary part κ of the material's complex index of refraction $n^* = n + i\kappa$, dubbed the extinction coefficient. Defining the attenuation coefficient as $\alpha = 4\pi\kappa/\lambda$, the relative decrease in light intensity I/I_o after traveling a distance x through a metal is given by[4]

$$\frac{I}{I_o} = e^{-\alpha x}$$

which is noted to be an exponential decay. This demonstrates the need to carefully regulate the thickness of ultrathin metal films in order to maintain transparency. However, making the films too thin can increase resistivity, creating a poor electrode. The Fuch-Sondheimer model gives the ratio of film to bulk resistivity ρ_f/ρ_b in terms of the ratio of film thickness to bulk mean free path in the material $c = t/l_b$ as[5,6]

$$\frac{\rho_f}{\rho_b} = \frac{4}{3}\frac{1}{c[\ln(1/c) + 0.4228]}$$

From this it can be seen that as the film thickness approaches the mean free path, resistivity increases. The two competing factors of transparency and conductivity necessitate the optimization of film thickness. A common measure of comparison between films is the Haacke's figure of merit, defined in terms of the transmittance T and sheet resistance R_s as[7]

$$\phi_{TC} = \frac{T^{10}}{R_s}$$

Additionally, though outside the scope of this work, the long-term stability of such films with thickness should also be taken into consideration.

In this work, ultrathin nickel films were produced on glass and undoped silicon substrates for testing of the relevant parameters of transmittance and resistivity. Transmittance spectra are obtained in a range spanning from UV to IR using an ellipsometer and infrared microscope, and resistivity is determined from sheet resistance measurements using a four-point probe setup. The results are analyzed to find the best film of those produced based on the Haacke's figure. In addition, fits to the data are performed and a relative slope method is used to find an optimal thickness based on equal weighting of transmittance and resistivity. Features of the transmittance spectra and resistivity are discussed and compared with findings from other sources.

II. EXPERIMENTAL

Nickel films with thicknesses varying by 1 nm in the range of 2-7 nm were independently deposited on glass and undoped silicon substrates using an electron-beam physical vapor deposition process under high ($< 10^{-8}$ Torr) vacuum. During deposition, the film thickness and growth rate were measured using a quartz crystal oscillator with a calibrated crystal thickness monitor. The deposition rate was maintained at approximately $1\,\text{Å}\,\text{s}^{-1}$ by controlling the electron beam current. This was performed in a class-1000 clean room and the nickel target was degassed before depositions to ensure the deposited film was free from contaminants. After deposition was complete, the films were dusted with nitrogen and no further processing steps were performed.

After deposition, the thicknesses were confirmed using a J.A. Woollam M-2000 ellipsometer in reflection mode with a preset model for nickel. The same ellipsometer was used in transmission mode to measure the transmittance spectra of the films deposited on glass substrates in the UV to near-infrared range. An uncoated substrate was also measured to obtain the glass transmittance for later isolation of the nickel spectra. For transmittance measurements in the short- to long-wavelength infrared range, a Bruker Hyperion 3000 Fourier Transform Infrared (FTIR) microscope was used in transmission mode with the films deposited on silicon substrates. The system was first calibrated to the correct beam intensity by comparison of the measured spectrum of an uncoated silicon sample to the known spectrum, adjusting the condenser aperture until the two closely matched. This calibration method has been previously verified[8]. The knife-edge aperture was adjusted so that a $100 \times 100\,\mu\text{m}$ area was measured. The spectrum for each thickness was measured at several different points to check for uniformity and to ensure a defective area was not imaged. As with the glass, a spectrum of an uncoated silicon substrate was recorded to isolate the nickel from it.

Electrical resistivity measurements were performed on the films with silicon substrates using a standard 4-point probe technique to obtain the sheet resistance of each film. Details of the method are described elsewhere[9]. A Keithley 2400 source meter supplying a current of 100 µA with a voltage compliance of 21 V was used to take the measurements. Testing was done multiple times at different locations for each sample to check consistency of the results. The resistivity of uncoated silicon was also checked and seen to be much greater that of any of the films, so it can be assumed to not contribute to the measured results.

III. RESULTS

The transmittances of the nickel films are shown in Figure 1 and Figure 2 with their respective thicknesses. Figure 1 depicts spectra obtained by the ellipsometer,

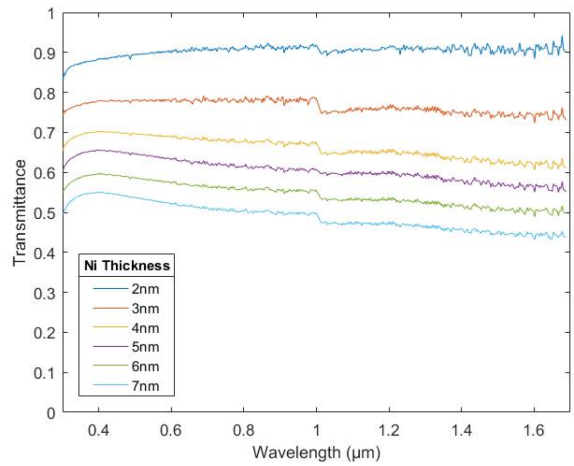

FIG. 1. Transmittance spectra of nickel films of various thicknesses in the UV to near-infrared range, measured using an ellipsometer in transmission mode. The spectra are isolated from that of their glass substrates.

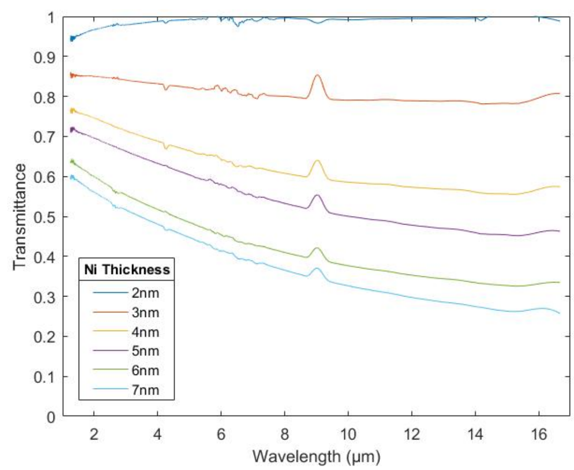

FIG. 2. Transmittance spectra of nickel films of various thicknesses in the short- to long-wavelength infrared range, measured using an ellipsometer in transmission mode. The spectra are isolated from that of their undoped silicon substrates.

and Figure 2 shows that from the FTIR microscope. The effects of substrates on transmittance were factored out by division of their spectra from those of the substrate and film combination. The spectra from the FTIR microscope were smoothed using a Savitzky-Golay filter to minimize noise resulting from infrared absorption by atmospheric gases; mainly carbon dioxide and water vapor. Taking the infrared region as the domain of interest, the average transmittances from spectra obtained by the FTIR microscope are averaged and listed by film thickness in Table 1.

The determined resistivity from sheet resistance measurements for each film thickness is also listed in Table 1. As a method of comparing film properties, the Haacke's

TABLE I. Table 1

Ni thickness (nm)	Average T	ρ (Ω m)	ϕ_{TC} (Ω^{-1})
2	97%	5.9×10^{-6}	2.5×10^{-4}
3	84%	2.0×10^{-6}	2.8×10^{-4}
4	73%	9.7×10^{-7}	1.7×10^{-4}
5	67%	7.3×10^{-7}	1.3×10^{-4}
6	57%	5.4×10^{-7}	4.2×10^{-5}
7	53%	4.4×10^{-7}	3.0×10^{-5}

figure of merit ϕ_{TC} is shown in the same table. The 3 nm film shows the highest Haacke's figure, and can therefore be claimed to be the best performing of the films produced.

In order to obtain a better estimate of the optimal film thickness, least squares fits were performed to the average transmittance and resistivity as a function of film thickness. The transmittance was fitted with a linear relation and is shown in Figure 3. The resistivity was fitted with a power law and is shown in Figure 4. Using the equations of fit, the point where the relative slope of both transmittance and resistivity were equal was found, signifying a balanced trade-off between the two with the assumption of equal weighting. This occurred at a thickness of approximately 3.3 nm, which is the determined ideal thickness.

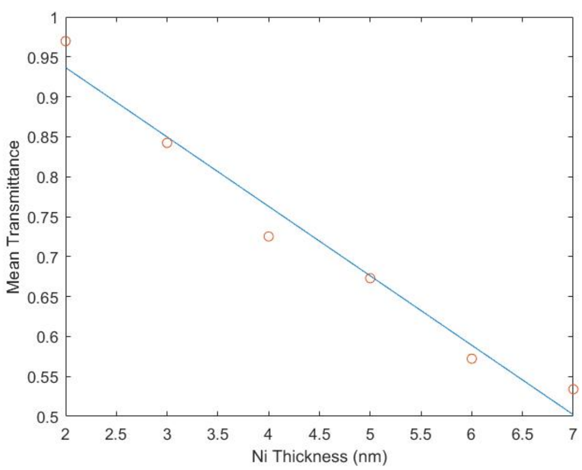

FIG. 3. Average transmittance of each film thickness in the FTIR-measured range. A line of equation $-0.0869x + 1.1104$ where x is the thickness in nm was fitted by least squares and is shown.

IV. DISCUSSION

The absorption of light in metal films, such as nickel, is seen to be highly dependent on the film thickness, with increases of only a few nanometers resulting in significant transmission losses. From Figures 1 and 2, it can be seen

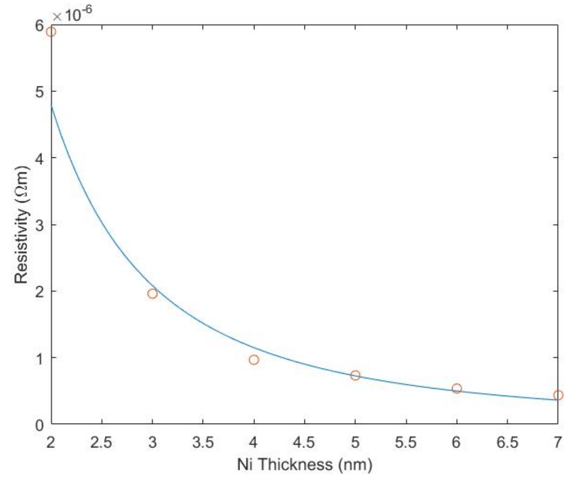

FIG. 4. Resistivity of each film thickness obtained by measuring sheet resistance using a four-point probe. A power law of equation $2^{-5}x^{-2.06}$ where x is the thickness in nm was fitted by least squares and is shown.

that the drop in transmission is smaller with successive increases in film thickness, confirming the expected exponential absorption behavior. Furthermore, as the spectra extend further into the infrared they can be seen to slope downward, as can be seen in Figure 2. This indicates a dependence of absorption with wavelength, with further absorption occurring at longer wavelengths. This can be explained as a result of the increasing extinction coefficient of nickel with wavelength, leading to higher absorption in the films[10]. Such films would not be suitable for use at longer wavelengths, as the increased absorption leads to significant transmission losses.

A comparison of transmittance with another source in similar wavelength ranges shows comparable performance for wavelengths near the visible spectrum[11]. However, for infrared wavelengths, the films produced here are seen to drop in transmittance more quickly. A possible reason for this is the deposition process used; electron-beam physical vapor deposition (EBPVD) as opposed to dc sputtering. EBPVD tends to produce less compact films as result of the low kinetic energy of particles ejected from the target compared to sputtering[12]. This leads to poorer layering of the film contributing to greater dislocation density, and a greater surface roughness. Both of these factors contribute to light scattering in the film so that is spends more time in the material, increasing the amount of absorption. This in turn results in greater transmission losses.

The resistivity of the films drops sharply with initial increases in film thickness, before beginning to level out as the thickness is increased further. This can be explained as the resistivity approaching that of the bulk material as thickness increases, with conduction being less limited by surface scattering as a result of the thickness being close to the mean free path of conduction electrons in the material. For the case of 2 nm thickness, the resistivity is seen to be an outlier from the general trend. A possible reason for this could be increased scattering from grain boundaries, increasing the resistivity further than thin film effects would alone. It is possible that with such a small thickness the film is not uniformly developed, with isolated grains still forming on the substrate's surface as the metal vapor precipitates during the deposition process. With further deposition these grains can increase in size and form more closely together, reducing electron scattering and decreasing resistivity.

Compared to nickel films produced by others, the ones examined here are seen to have a resistivity approximately an order of magnitude higher for a particular thickness. As with the discrepancies with transmittance from different sources, the difference in resistivity can be attributed to the use of EBPVD instead of dc sputtering to produce the films. As previously mentioned, EBPVD tends to create less dense films, and the lower degree of compacting results in a greater amount of defects present for the same thickness of film. These defects act as scattering sites for conduction electrons, lowering their mean free path in the material and therefore decreasing conductivity. This gives a greater resistivity compared to denser, more continuous films produced by a dc sputtering process.

V. CONCLUSION

In this work, the transmittance and resistivity of ultrathin nickel films of varying thicknesses were investigated, and an optimum thickness was found. As expected, transmittance and resistivity both increase with film thickness, necessitating an optimization between these two factors to obtain a film suitable for use as a transparent conductive electrode. By determining the Haacke's factor for each film, the 3 nm film was determined to be the best film produced for this purpose. A more precisely defined optimum thickness of 3.3 nm was found by assuming an equal weighting between transmittance and resistivity and using fits to the data obtained. Discrepancies between results obtained here and from other sources can be attributed to the different deposition methods used, since EBPVD produces a less dense film than dc sputtering.

VI. REFERENCES

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