J Mater Sci: Mater Electron (2009) 20:S181–S184
DOI 10.1007/s10854-007-9519-7

Ultra thin nickel transparent electrodes

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Received: 10 August 2007 / Accepted: 29 November 2007 / Published online: 22 December 2007

Abstract Transparent electrodes made of ultra thin metals have recently been demonstrated with performances comparable to those offered by transparent conductive oxides (TCOs), which are traditionally used in applications such as photovoltaic cells, light emitting devices, photodetectors and electro-optical modulators. In this work we report highly uniform, optically transparent and electrically conductive nickel films. Their good performance, combined with low cost and simplicity in processing, make ultra thin Ni films highly competitive, even with respect to the latest developments in TCO technology. Nickel films can be easily incorporated into an industrial process flow and could therefore be an attractive alternative to TCOs in many industrial applications.

1 Introduction

The optoelectronics industry has long demanded electrodes that are both optically transparent and electrically conductive. Transparent electrodes allow bringing charge collection to or from the active region with low optical loss. The state of the art solution consists in large band gap semiconductors doped with a metal, the so-called transparent conductive oxides (TCOs).

TCOs were the first materials to be used as transparent and conductive electrodes for optoelectronic devices because of their high optical transmittance as well as their good electrical conductivity. Electrical resistivities of the order of $10^3 \mu\Omega$ cm and optical transmittance in excess of 80% from the visible to the Near IR range are usually obtained [1–6]. However, TCOs characteristics are strongly related to the deposition method and to post-deposition treatments (such as annealings), requiring an accurate control of the concentration of dopants, vacancies and defects. Since it is not always straightforward to introduce post-processing into an industrial flow, we have searched for an alternative material for the fabrication of this type of transparent conductive electrodes.

A solution can be found in the use of purely metallic materials. Similar transmittance performances can actually be achieved in this case if the metal film thickness is low enough (down to a few tens of Å) [7–9]. Deposition of metallic films does not involve any complex treatment and can be easier to introduce into an industrial flow than TCOs. In addition, metals intrinsically show a significantly lower resistivity with respect to TCOs, even when they are very thin. It is possible to obtain transparent and conductive metallic electrodes by an appropriate choice of metal layer thickness.

The development of ultra thin films has always been limited by the minimum thickness one can achieve before the layer becomes discontinuous. High conductivity of the metallic layers indeed requires a good film continuity, which can be partly achieved by ensuring that the actual roughness of the layer is much lower than its thickness. The quality of obtained films depends on the metallic material,

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the substrate and conditions of deposition. Impurities and contaminants are likely to be the most important source of defects and discontinuities for ultra thin films. Thanks to the recent developments in ultra high vacuum deposition systems, it is possible to almost eliminate their presence. In this case continuity of deposited films depends only on kinetics of growth, which can be controlled to some extent to obtain films with a surface roughness of 10 Å or below [7, 9].

In this work we have successfully deposited by sputtering ultra thin Ni layers, that are both electrically conductive and optically transparent in a broadband wavelength range. When compared to a common TCO material, such as indium tin oxide (ITO), the Ni films show similar optical transmittance and larger electrical conductivity.

2 Deposition of ultra thin nickel films

The deposition technique used was DC magnetron sputtering at room temperature. Optimization and trade-off between fine control of thickness and kinetics of growth was carried out. Since roughness tends to increase at low deposition rates, process parameters had to be optimized to obtain homogeneous ultra thin thicknesses while keeping continuity. Moreover, special care was devoted to find a set of conditions giving rise to a solid, repeatable, industrial process (as explained in [7]), avoiding extreme limit conditions difficult to reproduce on large scale.

Polycrystalline Ni films have been deposited of thicknesses ranging from 20 Å up to 8,000 Å. Since the first aim of this study was to address the use of transparent electrodes for electro-optic applications and devices, $LiNbO_3$ substrates (X-cut wafers) were used for electrical and morphology characterization. Substrates of BK7 glass were used instead for optical characterization. The deposition was performed with a DC voltage sputtering machine *Kenosistec Dual Chamber* at room temperature and in pure Ar atmosphere. In all cases we used a DC power of 200 W and a pressure during deposition of 8×10^{-3} Torr. The resulting deposition rate was 1.6 Å/s. Such conditions were found to be the optimal for a robust and reproducible process for ultra thin films. Good uniformity, better than 8%, was routinely obtained on a 4 × 4 in. area. (Fig. 1)

Film thickness was measured by means of a profilometer (*KLA-Tencor P15*) for samples thicker than about 100 Å. For the thinnest Ni layers instead, thickness was inferred from the deposition rate [7].

3 Surface analysis

Surface analysis of the samples was carried out by means of atomic force microscopy (AFM). The critical parameter

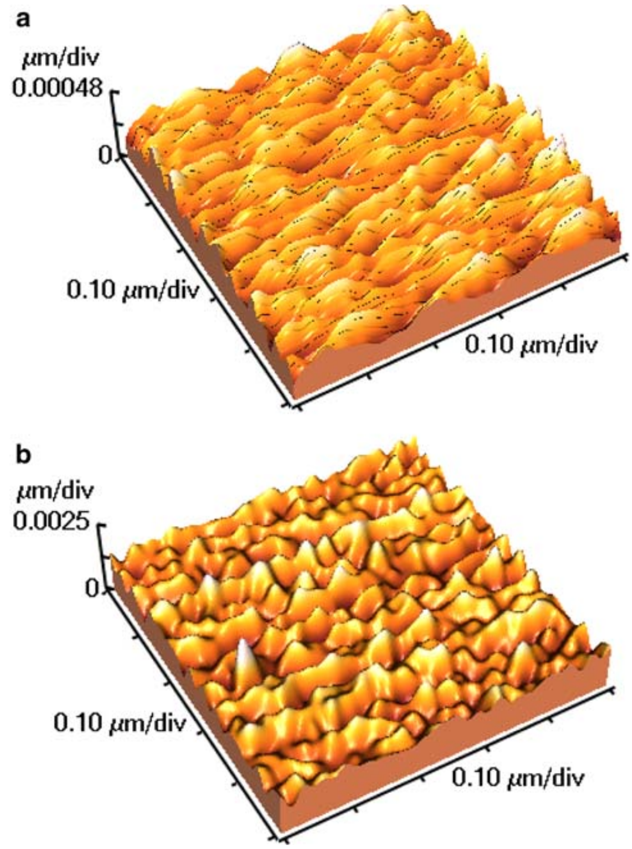

Fig. 1 AFM images of surface morphology. (**a**) Blank substrate before deposition, peak-to-valley 6 Å, RMS 0.8 Å. (**b**) Ni 22 Å thick layer, peak-to-valley 21 Å, RMS 5 Å

to investigate is surface roughness, since it determines the minimum thickness below which the film becomes discontinuous. Besides film continuity, a surface analysis may also provide useful information on morphology and structural properties of the polycrystalline film. When passing from bulk to thin films, effects of surfaces and grain boundaries become important and may significantly affect the electrical and optical properties of a material.

Analysis were performed using an AutoProbe M5 AFM (*Park Scientific Instruments*) associated with an appropriate analysis software to measure surface roughness in terms of Root-Mean-Square (RMS) and mean peak-to-valley values. Acquisitions were run in contact mode over 0.5 μm area at 0.5 Hz scan rate. The maximum roughness is reached by the thinnest Ni layer—22 Å nominal thickness—giving rise to a mean peak-to-valley roughness of 21 Å and RMS 5 Å (Fig. 1b). Contribution to surface roughness due to Ni can be evaluated by taking into account the superimposed roughness due to the substrate alone (Fig. 1a). Such results for surface roughness indicate that the minimum thickness for film continuity lays in the range 10–20 Å. At the same time they indicate that roughness of the sputtered Ni films is very low, remaining at an almost "atomic" scale.

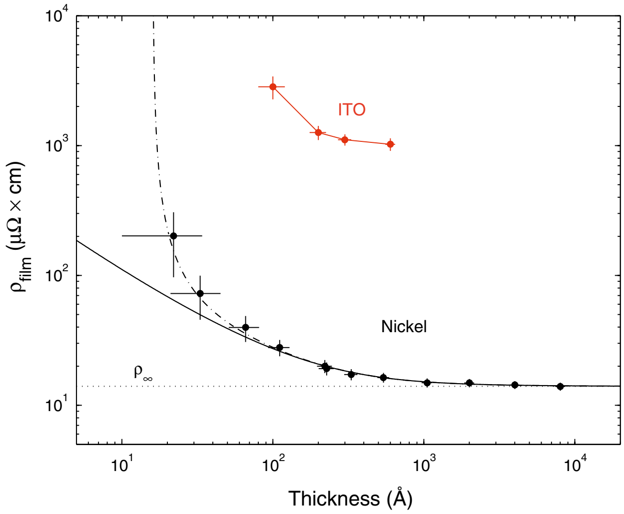

Fig. 2 Electrical resistivity of Ni as a function of film thickness. Curves: (solid line) FS model with $\rho_{\infty} = 14\ \mu\Omega$ cm and $l_{\infty} = 208$ Å; (dash-dotted line) same FS model improved with a film effective roughness of 15 Å. Typical ITO data is also plotted as a TCO reference

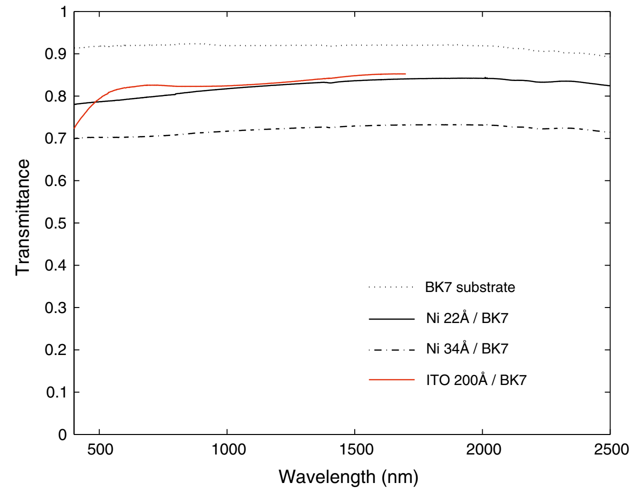

Fig. 3 Transmittance spectra of ultra thin Ni on BK7 substrate. Typical transmittance spectrum of annealed ITO thin film is also reported

Kinetics of growth is different for other metals such as aluminum, which is likely to be prone to a more significant island-like growth [7]. Over the minimum thickness, the intrinsic low surface roughness of Ni films is likely to keep an overall good continuity for the metal layer, with minor effects on the film cross-section. This fact was confirmed by resistivity measurements and subsequent analysis.

4 Electrical characterization

Resistivity of Ni films deposited on $LiNbO_3$ substrates was obtained by sheet resistance measurements using a classical four-points probe method. We used a *Keithley 2010* multimeter with a *Veeco FPP5000* four-points probe head. Figure 2 shows data points obtained for the Ni film resistivity as a function of thickness. At room temperature size-effect on resistivities of metal layers can be observed for thicknesses below 100 nm: as soon as film thickness becomes comparable to the electron mean free path, the resistivity of the metal film increases with decreasing thickness. This well-known phenomenon was first explained by Fuchs and Sondheimer (FS) [10, 11] as a size-effect due to scattering of conduction electrons on the plain surfaces of the film. In case of polycrystalline thin films this model needs some improvements. Namba [12] introduced the additional effects due to surface roughness; while Mayadas and Schatzkes [13] enlarged the model taking into account scatterings from grain boundaries. What we find is that the resistivity of our polycrystalline Ni metal layers remains consistent with that of a uniform and smooth film, until the thickness becomes of the same order as the layer roughness. The solid line of Fig. 2 shows the corresponding FS model with $\rho_{\infty} = 14\ \mu\Omega$ cm and $l_{\infty} = 208$ Å, where the parameters ρ_{∞} and l_{∞} are, respectively, the resistivity and the electron mean free path of an equivalent "infinitely thick" metal film. The scattering coefficient p was chosen equal to 0, assuming an entirely diffuse surface scattering. This model agrees very well with experimetal data only for thicknesses much larger than surface roughness. Indeed, a surface roughness causes an heterogeneous film thickness, reducing the effective cross-section useful for conduction. Assuming a 1D geometry with a total path L, the heterogeneous cross-section can be represented as $t = t(x)$ and the observed film resistivity at the mean film thickness t_m is actually an average over the local resistivities $\rho_{loc}(t(x))$:

$$\rho_{film}(t_m) = \frac{t_m}{L} \int_0^L \frac{\rho_{loc}(t(x))}{t(x)}\, dx$$

where $\rho_{loc}(t(x))$ should express the usual model for resistivity (FS or other).

The maximum variation in amplitude of the film cross-section is related to its peak-to-valley roughness. Following the same procedure we used in [7], we assumed a sinusoidal variation for the roughness profile and a simulation was performed with an "effective roughness" amplitude of 15 Å (dash-dotted line). This value should correspond to the minimum thickness at which the film remains continuous. The good agreement of this model with experimental data confirms that the effect of surface roughness dominates electrical conduction at ultra low thicknesses.

In the same plot ITO resistivity data are shown, as a reference for the TCOs. The reported data refer to ITO on $LiNbO_3$ (film thickness ranging from 100 to 600 Å), as we obtain in our laboratories. Notice that such resistivities are among the lowest compared to other data reported in literature [2, 14–16], even considering different substrates or different techniques. Despite this, Fig. 2 shows that for all thicknesses the resistivity of ultra thin Ni is lower than that of ITO.

The good agreement between experimentally observed resistivity data and FS theory improved with an "effective roughness" model may not be sufficient to confirm film continuity at ultra thin thicknesses. Quantum effects, like electron tunneling, are likely to become important and the presence of voids and discontinuities in the films cannot be ruled out only through a semi-classical interpretation of resistivity data. However, what is evident is that Ni films resistivity can be kept low through the control of the effective roughness, and that it can be much lower than that of ITO even at extremely thin thicknesses.

5 Optical characterization

As aforementioned, many optoelectronic applications require electrodes which are also optically transparent. Optical transmittances above 80% are routinely required for the state of the art TCOs.

Optical characterization of ultra thin Ni was performed on films deposited on BK7 substrates. We have measured the transmittance of samples, composed of the metallic layer and the BK7 substrate, using a wide range spectrometer (*Cary 500 Fourier Transform scan spectrometer*).

Results for ultra thin Ni on BK7 are reported in Fig. 3. Transmittance of the stack (film plus substrate) is plotted for wavelengths ranging from 400 to 2,500 nm. On the same plot is also reported a typical transmittance spectrum of annealed ITO thin film, as we obtain in our laboratories. At ultra thin thicknesses (less than 30 Å) Ni films exhibit transmittance similar to ITO. These features, combined with the low electrical resistivity demonstrated in the previous section, makes Ni films an interesting alternative to TCOs for optoelectronic devices, such as solar cells, light emitting diodes, photo-detectors, and integrated electro-optic modulators. Moreover, Ni transmission spectra are almost flat on a the whole range of wavelengths, from the visible to IR, showing a better performance with respect to TCOs which usually have a transmission window limited to 400–1,700 nm.

6 Conclusion

Ultra thin nickel films have been successfully deposited by DC magnetron sputtering on BK7, at room temperature and without any post-treatments. This is crucial in order to easily introduce them into a common industrial process and is one of the great advantages of ultra thin metal films over TCOs. Surface analysis, electrical and optical characterization of the samples have also been performed. The characteristics of the samples have been compared with state of the art TCOs, showing that electrical properties are clearly better than those of ITO layers, while still maintaining similar optical transmittance.

Acknowledgments The authors thank Davide Janner (ICFO) for his technical support and help and Cinta Pujol (Universitat Ramon Llull) for her special collaboration in the transmittance analysis. This work was partly supported by the Spanish National Program Plan Nacional no. TEC 2007-60185.

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