

# Widely transparent electrodes based on ultrathin metals

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Transparent electrodes made of single-component ultrathin (<10 nm) metal films (UTMFs) are obtained by sputtering deposition. We show that the optical transparency of the deposited films (chromium and nickel) is comparable to that of indium tin oxide (ITO) in the visible and near-infrared range (0.4–2.5  $\mu\text{m}$ ), while it can be significantly higher in the ultraviolet (175–400 nm) and mid-infrared (2.5–25  $\mu\text{m}$ ) regions. Despite their very small thickness, the deposited UTMFs are also uniform and continuous over the 10 cm substrate, as it is confirmed by the measured low electrical resistivity. The excellent optical and electrical properties, stability, compatibility with active materials, process simplicity, and potential low cost make UTMFs high-quality transparent electrodes for the optoelectronics industry, seriously competing with widely used transparent conductive oxides, such as ITO. © 2009 Optical Society of America  
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A crucial challenge in the optoelectronics industry is the realization of cheap and reliable transparent electrodes, i.e., films that permit one to bring electrical current or potentials in proximity of optically active regions without significant loss of optical energy. The state of art solution lies in large bandgap semiconductors heavily doped with metals, known as transparent conductive oxides (TCOs). TCOs show high transparency in the visible (VIS) range together with excellent electrical properties [1]. Among the TCOs, indium tin oxide (ITO) is the most widely used. It has been investigated for more than 40 years, thus resulting in an excellent trade-off between electrical resistivity and optical transparency. However, deposition of ITO films is far from being a straightforward process, since their electrical and optical properties depend on dopant concentration, defects, and vacancies and usually require postdeposition treatments. ITO can also lead to device degradation owing to indium and/or oxygen migration from  $\text{In}_2\text{O}_3$  into active organic layers [2]. Moreover, the ITO work function strongly depends on a cleaning procedure [3]. In addition, several optoelectronic devices such as ultraviolet (UV) photodiodes, UV LEDs, solar cells for space applications, or infrared (IR) pyroelectric detectors require electrodes with high transparency in the UV and/or IR regions. The typical band gap energy,  $E_g=3.75$  eV (331 nm), and plasma resonances in the near IR [1] make ITO impractical as transparent electrodes in the UV and IR, even when the free-electron density is changed significantly [4].

Metal films, when sufficiently thin (<10 nm), become transparent to light, still maintaining good electrical properties. In fact, metal-based transparent electrodes have been demonstrated using metal alloys [5], thin noble metals [6], alkaline earth metals protected from oxidation by noble metal layers [7],

multicomponent metals [8], and single-component ultrathin metal films (UTMFs) [9]. Single-component UTMFs based on transition metals, such as chromium (Cr) and nickel (Ni), can overcome the high cost of raw materials such as indium (In) and noble metals and can be grown using a simple single process technique, i.e., sputtering, thus becoming a straightforward solution to be integrated into typical industrial process flows. Contrary to TCOs, they possess high compatibility with nearly all organic and semiconductor materials (e.g., active medium) and related device fabrication steps.

In this Letter we show that Cr and Ni films deposited by single-step sputtering can be effective transparent electrodes over the entire wavelength range from the UV (175 nm) to the mid-IR (25  $\mu\text{m}$ ). In fact, a detailed comparison with ITO indicates a similar performance in the VIS range, while significant improvement is found in the UV and IR regions.

With the invention of ultrahigh vacuum technologies, it is now possible to deposit thin films with relatively lower impurities and contaminants, which would be the main causes of discontinuities and defects in ultrathin films. Polycrystalline Cr and Ni films of thicknesses of 2, 3.5, 5, and 10 nm were deposited by DC sputtering (Kenosistec Dual Chamber), at room temperature in a pure argon atmosphere of 8 mTorr with power levels of 200 W. It is already intuitive that the surface roughness of the substrate has to be smaller than the thickness of the metal film to be deposited if the latter is to be continuous. The UTMFs were grown on optically polished UV grade silica and silicon substrates of typical rms roughness levels below 1 nm being, respectively, used for UV–VIS and IR measurements. The thicknesses of the films were inferred from the deposition rates. Two different ITO films were also grown on UV grade silica and silicon substrates by *e*-beam evapo-

ration: 28 nm not annealed and 28 nm annealed at 450 °C in normal atmospheric conditions. In addition, we purchased another ITO sample (100 nm deposited onto Corning glass) for comparison. Transmittance spectra were taken with a PerkinElmer Lambda 950 spectrometer in the UV–VIS region whereas a Shimadzu FTIR-8400S Fourier transform IR spectrometer was used in the mid-IR range. Electrical resistivity measurements were carried out using a Cascade Microtech 44/7 S 2791 four-point probe system and a Keithley 2001 multimeter.

Figure 1 shows the average optical transmittance in the VIS range and the electrical resistivity for the Cr and Ni films of different thicknesses together with those of ITO layers, both not annealed and annealed. Note that substrate’s contribution is always taken

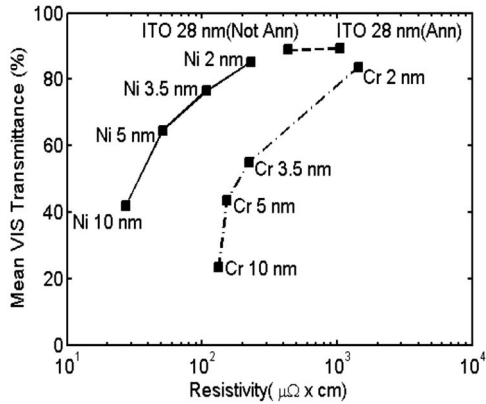


Fig. 1. Average optical transmittance in the VIS wavelengths against electrical resistivity for Cr and Ni films compared to ITO annealed and not annealed.

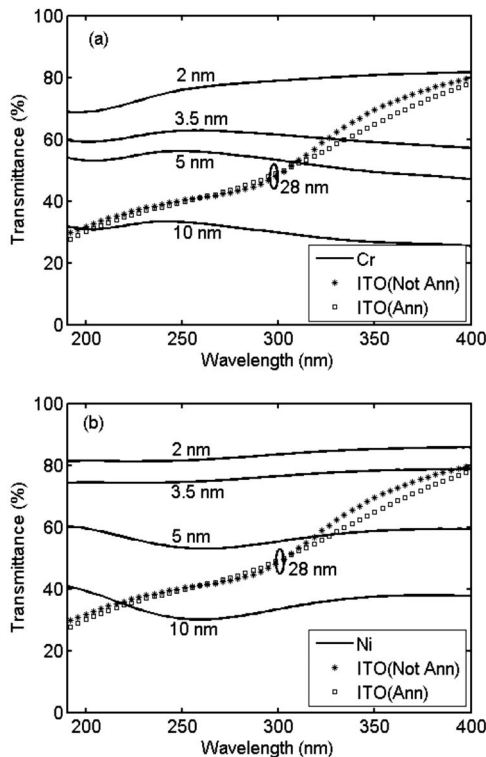


Fig. 2. Optical transmission of UTMFs compared to ITO annealed and not annealed in the UV region: (a) Cr and (b) Ni.

into account in optical transmittance measurements as  $T_f = T_t / T_s$ , where  $T_t$  is the total optical transmittance (film and substrate), whereas  $T_f$  and  $T_s$  are, respectively, the film and substrate optical transmittance. In the VIS range the performance of UTMFs is comparable to that of ITO. In fact, Ni films present a similar optical transparency with a significantly lower electrical resistivity. However, the real advantage of UTMFs over ITO in terms of optical transmittance is in the UV and IR ranges.

In the UV range (175 to 400 nm), ITO films present enhanced absorption and therefore reduced transmittance since the material bandgap is ~330 nm as discussed before. On the contrary, Cr and Ni films possess flatter optical transmittance with levels comparable to those in the VIS range [Figs. 2(a) and 2(b)].

Figures 3(a) and 3(b) show, respectively, the IR (from 2.5 to 25 μm) transmittance of Cr and Ni films, both being compared against ITO layers. As in the UV case, both Cr and Ni present superior optical transmittance properties: for thin samples both larger and flatter transmittance. We have also investigated the performance of ITO on Corning glass, which presents a much faster decay of the transmission in the near IR; in fact, the transmittance goes below 20% already at about 2.8 μm. The difference between the two ITO sets can be attributed to the difference in free electron density ( $n_e$ ) [4]. The fact that the lower near-IR transparent ITO (on Corning glass) has a higher free-electron density than that of ITO on UV fused silica or Si was also confirmed by

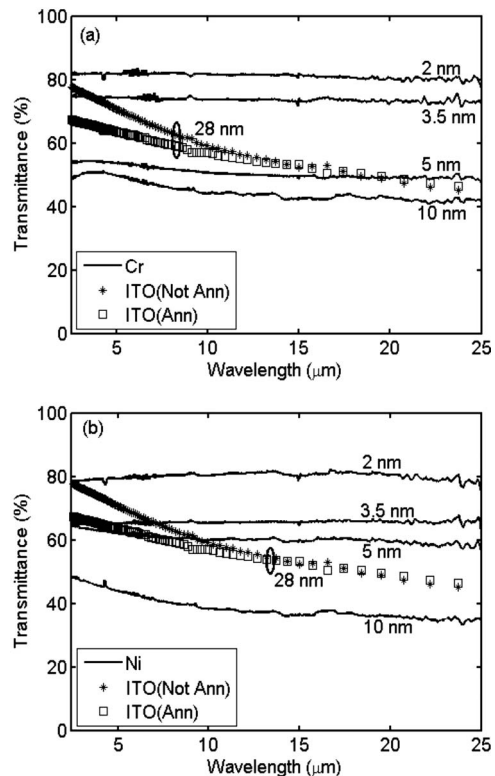


Fig. 3. Optical transmission of UTMFs compared to ITO annealed and not annealed in the mid-IR region: (a) Cr and (b) Ni.

its lower electrical resistivity: about  $160 \mu\Omega \times \text{centimeters}$  (the resistivity for ITO on UV fused silica was about  $430 \mu\Omega \times \text{centimeters}$ ).

A potential drawback of UTMFs is that their electrical behavior might change over time owing to the oxidation effect, thus undermining the functionality of the devices. In a recent paper, we have shown that one can in fact take advantage of the oxidation process to produce stable UTMFs [10]. An appropriate thermal treatment in the presence of oxygen (passivation) forms a top oxide layer that prevents further oxidation of the film. The resulting passivated UTMF has larger electrical resistivity and optical transmittance. As an example of UTMF passivation to stabilize the film, we have annealed the 10 nm Ni film at  $140^\circ\text{C}$  in ambient air for 4 h. After the treatment the film presents an electrical resistivity that is about twice the initial value, while its optical transmittance increases by about 2%.

After passivation, the film was subjected to an additional thermal treatment at  $90^\circ\text{C}$  for 2.5 h in ambient air. Both the transmittance and resistivity did not change significantly confirming that the film had already achieved stability.

We have carried out electrical resistivity measurements of a passivated 10 nm film as a function of temperature in the  $30^\circ\text{C}$ – $150^\circ\text{C}$  range (Fig. 4). The

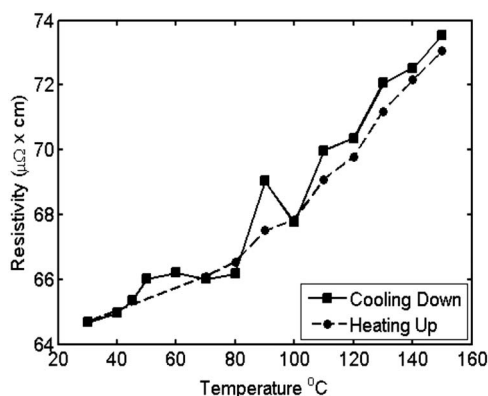


Fig. 4. Electrical resistivity variation of passivated 10 nm nickel film with temperature.

stability of the layer is confirmed by the absence of significant hysteresis, i.e., matching between “cooling-down” and “heating-up” curves. The calculated value of the temperature coefficient for the resistance ( $\alpha$ ) from Fig. 4 is  $0.0106^\circ\text{C}^{-1}$ .

In conclusion, we have successfully deposited UTMFs on UV fused silica and silicon substrates with high uniformity and continuity. Our results show that sufficiently thin Ni and Cr films are highly transparent over the full wavelength range, from the UV to the IR (175 nm to  $25 \mu\text{m}$ ), still maintaining high electrical conductivity. The measured wide optical transmission and excellent electrical properties, combined with the proven stability after an ad hoc passivation treatment, make UTMFs serious competitors to TCOs, such as ITO, in particular in the UV and IR ranges.

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