Applied Surface Science 269 (2013) 17–22

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Huge field-effect surface charge injection and conductance modulation in metallic thin films by electrochemical gating

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ARTICLE INFO

Article history:
Available online 9 October 2012

Keywords:
Field-effect experiments
Electrochemical gating
Surface electron states
Conductivity of metals

ABSTRACT

The field-effect technique, popular thanks to its application in common field-effect transistors, is here applied to metallic thin films by using as a dielectric a novel polymer electrolyte solution. The maximum injected surface charge, determined by a suitable modification of a classic method of electrochemistry called double-step chronocoulometry, reached more than 4×10^{15} charges/cm^2. At room temperature, relative variations of resistance up to 8%, 1.9% and 1.6% were observed in the case of gold, silver and copper, respectively and, if the films are thick enough ($\geqslant$25 nm), results can be nicely explained within a free-electron model with parallel resistive channels. The huge charge injections achieved make this particular field-effect technique very promising for a vast variety of materials such as unconventional superconductors, graphene and 2D-like materials.

1. Introduction

One of the milestones of the technological revolution that has occurred in the last 50 years is the invention of the field effect transistor (FET). As it is well known, the working principle of FET devices is based on the modulation of the transport properties of a material by means of an applied electric field. This is important not only from a technological point of view but also from a fundamental one. Indeed, field-effect experiments allow tuning the charge density of a material without the side effects typical of chemical substitutions or application of pressure, such as introduction of disorder or modification of the lattice structure. In this regard field-effect experiments allowed, for instance, enhancing the critical temperature of some superconductors [1–3], inducing metallic behaviour in insulators [4], a metal-to-insulator transition in a colossal magnetoresistive manganite [5] or even a superconducting phase transition in materials like $SrTiO_3$ [6], ZrNCl [7], and $KTaO_3$ [8]. In order to achieve large effects, a high amount of charge has to be injected and therefore very intense electric fields are required. Instead of using the standard solid dielectric which is nowadays a very common solution for commercial devices, the use of a polymer electrolyte solution (PES) [4–10] is a very promising technique to achieve these huge charge injections. With a solid-dielectric device it is possible to induce a surface charge n_{2D}^{max} of the order of 10^{13} charges/cm^2 while with polymeric gating techniques this value can easily reach some units in 10^{14} charges/cm^2 as a consequence of electric fields as high as 100 MV/cm. By using a suitable PES, Dhoot et al. have recently achieved the unprecedented surface density of injected charge of 2×10^{15} charges/cm^2 [5]. The electrochemical gating technique is based on the formation of an electric double layer (EDL) between an electrolyte solution and the surface of the sample under test: the polymer solvates positive and negative ions in the electrolyte solution and an external bias drives them towards the oppositely polarised surface of the film or gate, thus forming the EDL. Therefore, the EDL acts as a parallel-plate capacitor with extremely small distance between the plates (of the order of the polymer molecule size) [7] and thus a very large capacitance.

As already stated above, field-effect experiments have been performed in some exotic materials in order to induce dramatic modifications of their properties or even phase transitions [3]. However, although poorly studied, field-effect measurements have been carried out also in metals. The little interest in this topic is mainly due to the fact that it seems not to be so much attractive from an applicative point of view, but also because the effect is commonly considered to be difficult, or almost impossible, to observe: indeed, the electronic screening length in the semiclassical model for a metal is less than one atomic radius. Nevertheless, field-effect induced modulations of the conductivity in metals have already been observed in the past [1,11–16], also justifying a fundamental interest in this subject.

Here we report on field-effect experiments performed on gold, silver and copper by means of the electrochemical gating technique. The novel PES we adopted allows surface charge injections as high as 3–4 × 10^{15} charges/cm^2 [16] (thus even larger than those obtained by Dhoot et al. [5]) and far-from-negligible modulations

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http://dx.doi.org/10.1016/j.apsusc.2012.09.157

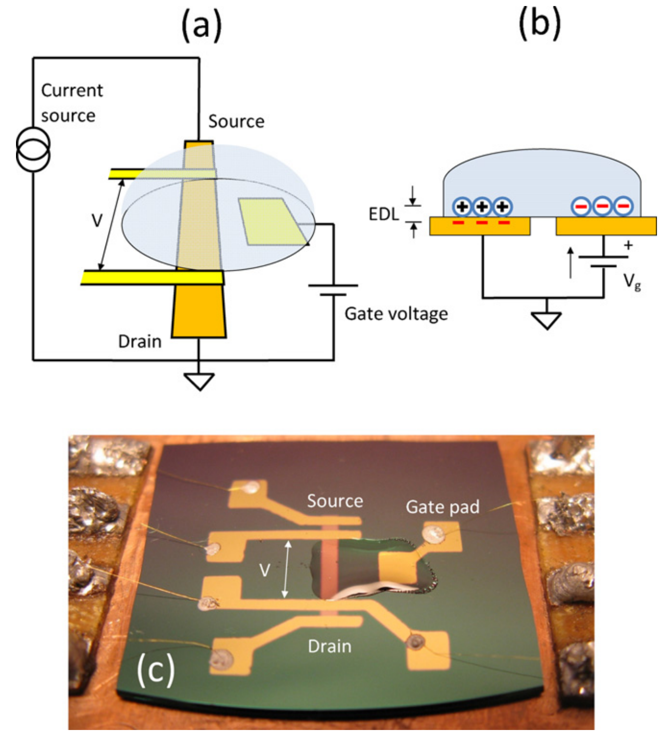

Fig. 1. (a) Scheme of devices for electrochemical gating: the portion of the film between the voltage contacts is covered by the PES that is polarised by a voltage source (V_{gate}). The film resistivity is measured in the standard four-probe configuration. (b) Cross-section sketch of the device: when V_{gate} is applied, ions are accumulated at the interface with the metallic film and a charge with opposite sign is induced on its surface, forming an EDL. (c) Photograph of a typical device used in our field-effect experiments on metallic thin films.

of the conductivity were observed in all the investigated metals. In particular, relative variations of the resistivity $\Delta R/R'$ up to 8%, 1.9% and 1.6% were achieved at room temperature in gold, silver and copper, respectively. If films are not too thin, such as to avoid a dominant role of surface scattering, the trend of $\Delta R/R't$ as a function of n_{2D} (where t is the thickness of the film) can be nicely explained within the free-electron model. Moreover, the huge surface charge injections achieved make this technique promising for many other materials such as graphene, unconventional superconductors and 2D-like crystals.

2. Experimental setup

Fig. 1(a) shows a sketch of the experimental setup. The device, fabricated in the planar configuration as in Ref. [10], consists of the metallic thin film under study, the gate pad and the PES. Thin films are obtained by physical vapour deposition (PVD) of the selected metal (gold, silver or copper) at a pressure $P \sim 2 \times 10^{-5}$ mbar. Their thickness is measured by means of atomic force microscopy (AFM) which is also used to investigate the morphology of the film surface, together with field-emission scanning electron microscopy (FESEM) [16]. To account for the possible presence of voids between grains that can reduce the effective cross sectional area of the film, we also applied a correction proposed by Rowell [17] and based on the fact that the temperature dependence of the resistivity depends only on the material and not on the form of the sample (bulk, polycrystal, film). The procedure requires comparing the experimental $\rho(T)$ of a given film with the resistivity of the pure (bulk) material, and provides a scaling factor F for the geometrical cross section. In most Au films, we found out that $F \simeq 1$, i.e. there is no need of correction and the geometrical cross section coincides with the effective one. In all the Cu and Ag films, instead, the correction was necessary, which is consistent with AFM and FESEM images that show a greater roughness. An example of AFM image on a Ag film and the corresponding z-profile to determine its thickness is shown in Fig. 2.

Voltage, current and gate pads were deposited on top of the film by evaporating gold, independently of the metal under study. As a substrate, we adopted either glass, or amorphous SiO_2 or Si_3N_4 on a Si wafer.

The metallic thin film behaves as the channel of a standard FET whose resistivity is measured with a standard four-probe configuration by inverting the current during each measurement or by using the ac technique. The PES acts as the dielectric and is therefore connected on one side to the metallic film and on the other side to the gate pad. A bias is applied to the gate by means of a source-measure unit that, at the same time, measures the electric current flowing through the PES. The PES we used was obtained by a reactive mixture of bisphenol A ethoxylate (15 EO/phenol) dimethacrylate (BEMA; average Mn: 1700, Aldrich), poly(ethylene glycol)methyl ether methacrylate (PEGMA; average Mn: 475, Aldrich), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in the presence of 3 wt% of a 2-hydroxy-2-methyl-1-phenyl-1-propanon free radical photoinitiator (Darocur 1173, Ciba Specialty Chemicals). The quantities of BEMA and PEGMA are in a 3:7 ratio, and the LiTFSI is the 10 wt% of the total compound. The PES was then polymerised by UV exposure using a medium vapour pressure Hg UV lamp, with a radiation intensity on the surface of the sample of 30 mW/cm^2. All the above operations were performed in the controlled Ar atmosphere of a dry glove box with O_2 and H_2O content <0.1 ppm. Since the PES used here was originally developed for Li-ion battery applications, the reproducibility of its chemical and physical properties was widely tested by means of conductivity measurements, crosslink density measurements, thermal history and cyclic voltammetry [19]. A careful preparation according to the above recipe results in a very high reproducibility and stability of the PES over long times (several months).

Fig. 1(b) shows how the field-effect experiments work: the application of the gate voltage causes an accumulation of charge at the interface between the film and the PES, thus forming the EDL. A symmetric amount of charge is induced at the gate pad, shown on the right hand-side of Fig. 1(b). Fig. 1 (c) shows a photo of a real device used in these experiments.

3. Experiment and models

In this section we describe the measurements performed on the devices previously shown, as well as the models used to determine the injected surface charge and to quantify the effect of surface doping on the conductivity of the metallic thin films.

The sequence of operations and measurements performed on a single device is summarised in Fig. 3. At $t = 0$ a voltage is applied between the gate pad and the film. After a proper time (of the order of several hundreds of seconds due to the rather slow dynamic of the PES) this voltage is removed as shown in Fig. 3(a). A sharp peak in the gate current flowing through the PES appears immediately after the application of gate voltage, indicating the formation of the EDL. This current decreases almost exponentially and after a few seconds it reaches a very small constant value. When the gate voltage is removed a similar peak appears with negative values of the current, indicating the disruption of the EDL (Fig. 3(b)). The time integral of this gate current as function of time (Fig. 3(c)) provides the total amount of charge that flows through the PES and, by applying a proper procedure, allows extracting the (smaller) charge that is involved in the formation of the EDL. Finally, this dynamical formation and destruction of the EDL with the consequent charge injection at the surface of the metallic thin film gives rise to