# Electric field gating with ionic liquids

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The authors show that ionic liquids are well suited to specialized electric field gating applications in which large surface charge densities can be induced on the surfaces of low-carrier density thin-film metals. Using either coplanar or overlay gate configurations, they demonstrate field-induced resistance changes on the order of a factor of $10^4$ for thin conducting $InO_x$ films. The areal capacitances and field effect mobilities noticeably exceed those that can be achieved using $AlO_x$ dielectrics. In addition, the charge state can be frozen in by reducing the temperature, thus providing an opportunity for electric field tuning of metal-insulator transitions in a variety of thin-film systems. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2437663]

Field effect transistors (FETs) and related field-gated devices play a dominant role in our present day electronic and optical technologies. The semiconductor silicon and its native oxide[1] are the core components of such devices, sustaining a thriving electronics industry that is responsible for many of the consumer and military products dominating our present day economy. There are, however, important niche applications in which it is desirable to electric field gate organics, polymers, nanocomposites, complex oxides, and/or low carrier density metals for a multiplicity of applications including displays, sensors, actuators, low cost memory, etc. Depending on the application, the choice of components for a field-gated device can depend critically on cost, durability, speed of operation, impedance, transconductance, and extent of modulation of the film between the source and drain. In response to these challenges, one promising and well studied area of investigation is the use of electrochemical techniques to study surface resistance changes at the interface between a conducting film and an electrolyte.[2] Field gating effects utilizing electrolytes as the gate dielectric have been observed in nanotube based FETs,[3,4] organic electrochemical transistors,[5,6] and electrochemically induced resistance changes of porous nanocrystalline Pt.[7]

In this letter we report on the use of ionic liquids (ILs) rather than ionic fluid electrolytes as field gate dielectrics and show that a significant field-gate effect on thin films of amorphous composite $InO_x$ can be obtained utilizing rather simple gated source-drain configurations. Ionic liquids are highly polar low-melting-temperature binary salts typically comprising nitrogen-containing organic cations and inorganic anions. Since there is no solvent, ILs are distinctly different from aqueous, organic, gel, or polymer electrolytes. Ionic liquids advantageously have high thermal stability, they are nonvolatile, they are compatible with most materials systems, they can be exposed to moderate potential differences without undergoing redox reactions, and they are fluid over a wide temperature range. Ionic liquids have also been shown to manifest notable performance advantages when used as electrochemical mechanical actuators, electrochromic windows, and numeric displays.[8]

With respect to electric field gating, Wu *et al.* have demonstrated the use of ILs to modulate both the spectral transmittance and the resistance of single wall carbon nanotube films.[9] For porous materials with high surface to volume ratios, such as nanoporous metals[7] or nanotube mats,[9] liquid dielectrics can provide efficient coupling to most of the gated material. On the other hand, if the gated material is a nonporous continuous thin metal film such as low carrier density $InO_x$,[10] then excess charge at the electrochemical interface is screened within the metal on a distance on the order of atomic dimensions, and the resistance change is therefore only significant when the carrier density is low and the thickness of the sample is on the order of the mean free path of the conduction electrons. As we will see below, the advantage of using IL dielectrics compared to solid state dielectrics is a significantly enhanced charge modulation for the same gate voltage. This enhancement, which is due to the large double layer capacitance that occurs at the interface of the metal with the IL, is found to be significantly larger than obtained in previous work[10] using similar $InO_x$ films in combination with thin-film $AlO_x$ gate dielectrics. The compensating disadvantage is a significantly slower relaxation time.

The source and drain contacts of our test structures, separated by 1 mm and comprising 300-Å-thick Au deposited on 50-Å-thick Cr, were first evaporated onto clean glass substrates. The amorphous composite $InO_x$ films were then deposited at a rate of 1 Å/s through shadow masks using reactive ion beam sputter deposition.[10] The $InO_x$ films are stable in air, smooth textured, and semitransparent with carrier (electron) densities on the order of $5\times10^{19}$ cm$^{-3}$. For each deposition two samples were made: one for the field gating experiments and the other for Hall measurements. Both coplanar [Fig. 1(a)] and overlay [Fig. 1(b)] gate configurations were used. The IL chosen for our experiment was 99.5% pure 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-Beti) purchased from Covalent Associates. No systematic attempt was made to optimize the choice of IL, although careful efforts were made to keep the substrates and liquid containers clean and free of contaminants.

The dielectric relaxations of ILs, which typically cover a large range of frequencies,[11] can become particularly sluggish as the temperature is lowered. We study the trade-off between charging and relaxation time by using a Solartron model 1260 frequency response analyzer (FRA) to measure

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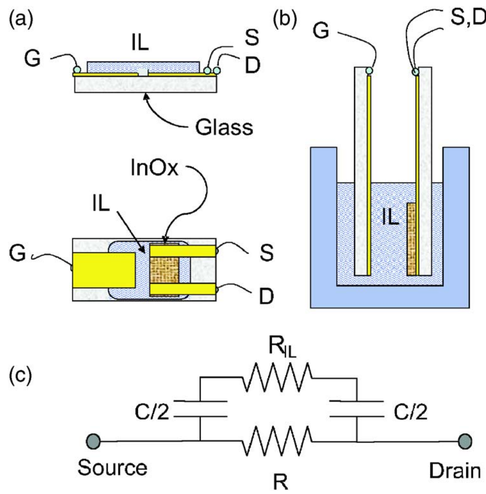


FIG. 1. (Color online) Coplanar (a) and overlay (b) gate configurations showing the placement of the gate electrode (G), the ionic liquid (IL), and the active $InO_x$ thin film connected between source (S) and drain (D) terminals. (c) Circuit model describing the capacitive coupling between the $InO_x$ film with resistance $R$ and the ionic liquid with resistance $R_{IL}$.

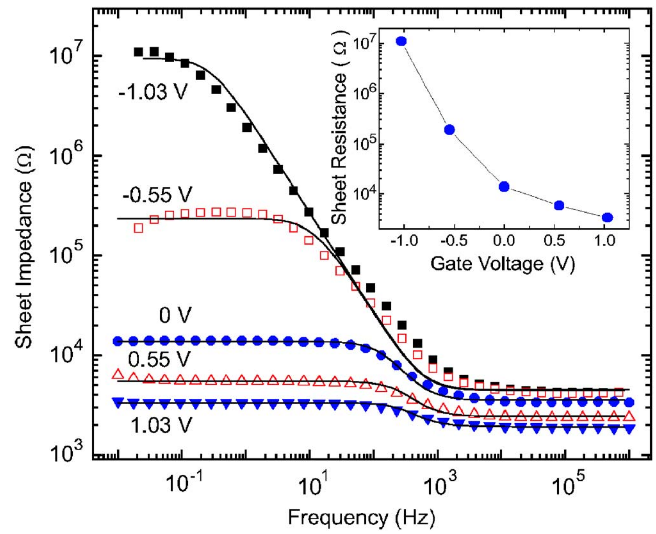


FIG. 2. (Color online) Frequency dependence of the magnitude of the sheet impedance at the indicated gate voltages. The coplanar configuration shown in Fig. 1(a) was used. Each sweep starting at the low frequency end takes about 30 min of measurement time for a constant source-drain voltage amplitude of 0.5 V rms. The solid curves are the fits using the circuit model of Fig. 1(c). Inset: Plot of the low frequency (0.02 Hz) resistance vs gate voltage for the same 40-Å-thick film shown in Fig. 2.

the gate voltage dependence of the complex impedance of a 40-Å-thick $InO_x$ film over the frequency range of $10^{-2}$–$10^{6}$ Hz. Since the pressed indium contacts to the source and drain terminals had a low contact resistance, the FRA was used in a two-terminal mode in which an ac voltage of fixed amplitude is applied between the source and the drain and the resulting phase-shifted current detected with a sensitive current amplifier. For these measurements we used the coplanar gate configuration of Fig. 1(a), which has the convenience of needing only a small amount of fluid to cover both the gate and the 3 $mm^2$ active area between the source and drain. The most efficient charge coupling occurs when the areas of the gate and the area of the active film between source and drain are approximately equal.[9] The frequency dependence of the magnitude of the impedance $|Z(\omega)|$ is shown in Fig. 2 for the indicated gate voltages $V_g$. Corresponding data for the phase angle are not shown. Linearity of the source-drain voltage with the source-drain current was verified at 1 Hz. The data show an increase/decrease of impedance for negative/positive gate voltages, thus indicating that the $InO_x$ film has negative carriers. This is well known from previous work[10] but was also checked for the 40-Å-thick film under consideration here by Hall measurements where the room-temperature carrier density $n=5.6\times10^{19}$ $cm^{-3}$ for field sweeps up to 7 T was found.

Two additional aspects of these data should be noted. First, there is a large asymmetry manifested by the significantly larger changes in impedance for negative $V_g$ (electron depletion) compared to positive $V_g$ (electron enhancement). Second, there is pronounced frequency dependence due to the low ionic mobilities in the dielectric fluid; equilibrium for electron enhancement occurs in ~100 ms (10 Hz) but for electron depletion (with concomitantly large changes in impedance) equilibrium occurs in ~100 s (0.01 Hz). Insight into this behavior is gained by analyzing the circuit model shown in Fig. 1(c). The model treats in a rather simplified manner the capacitive coupling between the $InO_x$ film with resistance $R$ and the ionic liquid with resistance $R_{IL}$. The magnitude of the impedance between the source and the drain for this model can be readily calculated as

$$|Z(\omega)| = \sqrt{\frac{(RR_{IL}\omega^2C^2(R+R_{IL})+R)^2+(R^2\omega C)^2}{(\omega^2C^2(R+R_{IL})^2+1)^2}}, \qquad (1)$$

which reduces to $R$ in the low frequency limit and to $RR_{IL}/(R+R_{IL})$, the parallel combination of $R$ and $R_{IL}$, in the high frequency limit. Using the $V_g=0$ data (solid circles of Fig. 2), we find a good fit (solid line) to Eq. (1) for $C=0.178$ $\mu$F. We then make the reasonable assumption that $C$ is independent of $V_g$ and find that Eq. (1) describes well the shape of $|Z(\omega)|$ for all of the curves shown in the main panel of Fig. 2. From these fits, $R_{IL}$ is found to be near constant at $1520\pm80$ Ω. It is somewhat surprising and yet satisfying that the simple model described by Eq. (1) works so well: the distributed capacitance along the $IL/InO_x$ interface is represented by just two series-connected capacitors, $R_{IL}$ is independent of $V_g$, negligible current is drawn by the gate voltage, and dielectric dispersion in the IL has been ignored.

In the inset of Fig. 2 we plot the gate voltage dependence of the 'equilibrium' low frequency (0.02 Hz) values of $R$ extracted from the data in the main panel. The asymmetry of the curve arises because the depletion of charge (negative $V_g$) close to the metal-insulator transition has a larger effect on the resistance than does the accumulation of an equivalent amount of charge (positive $V_g$). We calculate from the model fit value $C=0.178$ $\mu$F and the 3 $mm^2$ active area between the source and drain an areal capacitance $C/A=5.9$ $\mu F/cm^2$. For $V_g=1$ V, we find an areal charge density $N_{FE}=CV_g/eA$ $=3.7\times10^{13}$ $cm^{-2}$, where $e$ is the charge of an electron. In contrast to this field effect (FE) measurement, the Hall measurement result, $n=5.6\times10^{19}$ $cm^{-3}$, for the 40-Å-thick film implies $N_{Hall}=2.2\times10^{13}$ $cm^{-2}$. Thus $V_g=-1$ V across the IL is sufficient to drive the $InO_x$ film nearly into the fully insulating state as seen experimentally.

Compatibility of the FE and Hall mobilities, $\mu_{FE}$ and $\mu_{Hall}$, is also quite satisfactory. To calculate $\mu_{FE}$, we use the Boltzmann expression[10] $\mu_{FE}=3A(\partial G/\partial V)/2C$ and evaluate

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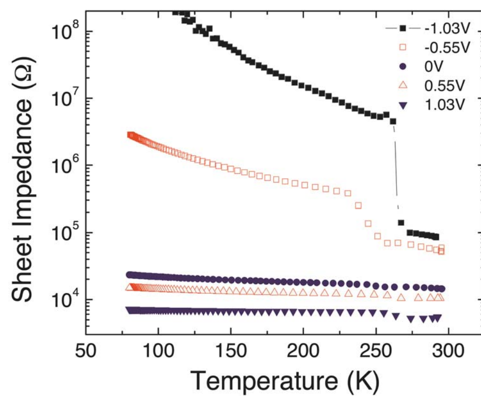


FIG. 3. (Color online) Temperature dependence on slow cooling of the magnitude of the impedance at the gate voltages shown in the legend. The 40-Å-thick film was mounted in the overlay configuration shown in Fig. 1(b). Measurements are taken at 10 Hz for a constant source-drain voltage amplitude of 0.05 V rms.

$\partial G/\partial V = 1.47\times 10^{-4}$ S/V by taking the odd part of the dependence of the conductance $1/R$ on $V_g$, where $1/R$ is calculated directly from the resistances of the inset of Fig. 2. The result, $\mu_{\mathrm{FE}} = 37.3$ cm$^2$ V$^{-1}$ s$^{-1}$, compares favorably with $\mu_{\mathrm{Hall}} = 1/eN_{\mathrm{Hall}}R = 20.6$ cm$^2$ V$^{-1}$ s$^{-1}$.

The areal capacitance discussed above for ionic liquids is comparable to the 5 $\mu$F/cm$^2$ obtained using solution-processed solid polymer electrolytes as dielectrics for organic thin film transistors.[12] These electrolytic dielectrics also exhibit a slow ionic response time which manifests itself as pronounced hysteresis when the gate voltage is swept too rapidly.[12]

The large gate induced charge densities associated with IL dielectrics can be frozen into place by simply cooling the sample through its glass transition $T_g$ with the gate voltage on. We demonstrate this electric field poling in the $|Z(\omega)|$ plots of Fig. 3 for a second 40-Å-thick sample. The overlay gate configuration of Fig. 1(b) prevented any accidental spillage of IL in the cryostat and also accommodated thermal contraction. We used a measuring frequency of 10 Hz during the temperature sweeps, a frequency which was low enough to assure that most of the charge was transferred and fast enough to follow the resistance changes as the sample cools through $T_g \sim 250$ K. The jumps in $|Z(\omega)|$, which are especially pronounced for negative $V_g$, occur as the IL freezes and $R_{\mathrm{IL}}$ increases to a large value so that by Eq. (1), $|Z(\omega)| \rightarrow R$. At this point the measured resistance of the $\mathrm{InO}_x$ film is unaffected by ac shunts through the capacitatively coupled IL. At these low temperatures removing the gate voltage has no effect on the charge state, and the sample remains poled for all $T < T_g$. Thus for $T < T_g$, the gate induced charge is frozen in place and the continued increase in resistance is an intrinsic property of the electron depleted $\mathrm{InO}_x$.

Previous work on field gating of comparable thickness $\mathrm{InO}_x$ films using thin-film ion-beam sputter deposited $\mathrm{AlO}_x$ as the gate dielectric reported typical areal capacitances of 0.5 $\mu$F/cm$^2$ and typical field effect mobilities of 3.0 cm$^2$ V$^{-1}$ s$^{-1}$.[10] As we have seen above, the use of IL dielectrics provides an approximate factor of 10 improvement in areal capacitance and a field effect mobility comparable to the 10 cm$^2$ V$^{-1}$ s$^{-1}$ value reported for mylar foil dielectrics on $\mathrm{InO}_x$.[13] Trapping of charge and additional surface scattering at the IL/$\mathrm{InO}_x$ interface do not appear to be significant, since these mechanisms would reduce the mobility. Accordingly, these two improvements combine to give a significant performance advantage when ILs are used in field gating applications that do not require a fast response time. We anticipate that the techniques described here and demonstrated for thin $\mathrm{InO}_x$ films will be useful in fundamental studies of strongly correlated systems, such as manganites and high-$T_c$ superconductors, where electrostatic field doping can substitute for chemical doping in the vicinity of the metal-insulator or superconductor-insulator transition. Advances in this direction have already been made with dielectrics such as micromachined $\mathrm{SrTiO}_3$ single crystals.[14] Ionic liquids may also be useful for electrochemical doping of conducting polymers and lead to higher mobilities than seen, for example, in field gating experiments using liquid electrolytes (0.1$M$ propylene carbonate solution of tetraethylammonium tetrafluoroborate) on regioregularpoly(3-hexylthiophene) thin film transistors.[6]

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