Probing near-interface ferroelectricity by conductance modulation of a nano-granular metal

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Abstract
The electronic functionality of thin films is governed by their interfaces. This is very important for the ferroelectric (FE) state which depends on thin-film clamping and interfacial charge transfer. Here we show that in a heterostructure consisting of a nano-granular metal and an organic FE layer of [tetra-thiafulvalene]$^{+3}$+[p-chloranil]$^{-5}$ the nano-granular layer’s conductance provides a sensitive and non-invasive probe of the temperature-dependent dielectric properties of the FE layer. We provide a theoretical framework that is able to qualitatively reproduce the observed conductance changes taking the anisotropy of the dielectric anomaly at the paraelectric–FE phase transition into account. The approach is also suitable for observing dynamical effects close to the phase transition. Focused electron beam induced deposition as fabrication method for the nano-granular metal guarantees excellent down-scaling capabilities, so that monitoring the FE state on the lateral scale down to 20–30 nm can be envisioned.

Keywords: ferroelectric thin films, nano-granular metals, focused electron beam induced deposition

1. Introduction

It is thin films and, in particular, their interfaces that define the electronic functionality of devices. This is an established fact in inorganic semiconductors as has been demonstrated for oxides in recent years [1]. The ferroelectric (FE) state provides important functionality in this regard, since the ability to switch the electric polarization by an electric field is the basic property needed in FE random access memories or field effect transistors [2]. The paraelectric (PE) to FE phase transition at the Curie temperature $T_C$ is equally important in basic research, since it is one of the most representative phase transitions in solids.
For both, applied and basic research, the ability to tune the PE–FE transition to a large degree is very attractive. How can this tuning be accomplished? Two mechanisms are particularly suitable for thin film structures, namely clamping effects and interfacial charge transfer. Clamping effects occur, if a thin film strongly adheres to a bulk substrate and follows its elastic response, e.g., thermal expansion effects in the consequence of temperature changes. Interfacial charge transfer is governed by the interfacial electronic states which form when the thin film is deposited on a substrate surface or as part of a multi-component heterostructure. Organic FE from the class of charge transfer systems (CTS) are ideal model systems in this regard [3, 4], since their reaction to clamping effects and charge transfer over the interface is particularly strongly pronounced [5–8]. This is so because their thermal expansion coefficients are about an order of magnitude larger than those of oxides [9] and their FE properties are governed by intermolecular charge transfer between a donor and an acceptor molecule rather than simple displacement of static point charges on the molecules. This gives rise to an electronic FE polarization which is much stronger than it would be expected for a simple displacive type FE state [10]. At the same time they are multiferroics, since with the onset of FE also a one-dimensional antiferromagnetic state is formed [11].

An important question in analyzing the FE state close to interfaces is: how can the influence of clamping and charge transfer be monitored, ideally in a way that does not interfere with the FE state itself? This is the starting point of the work presented here. We introduce a novel concept for monitoring the FE state in thin films with large sensitivity to the near-interface region. We show that strong modulations in the Coulomb charging energy in a nano-granular metal occur, if this is in close proximity to a FE thin film. These modulations lead to easily detectable changes in the electrical conductance which thus becomes a minimally invasive probe of the FE state, its temperature and electric field dependence, as well as its dynamic properties.

We demonstrate the monitoring effect for a bilayer thin film structure (see schematic in figure 4) consisting of the organic FE [tetraethylfulvalene]^{+\delta}[p-chloranil]^{-\delta} (TTF-CA) and a Pt-based nano-granular metal (Pt(C)) prepared by focused electron beam induced deposition (FEBID). TTF-CA is an organic CTS that shows a PE–FE phase transition at 81 K [14]. It consists of one-dimensional, mixed stacks of the donor (D), TTF, and the acceptor (A), CA (see inset of figure 1). The degree of charge transfer $\delta$ is about 0.2 from D to A in the PE phase and increases by a first order phase transition to about 0.7 in the FE state. With the PE–FE phase transition a dimerization of the D/A-pairs is associated leading to a multiferroic ground state in which, in addition to the FE state, a one-dimensional dimerized antiferromagnetic spin $S = 1/2$ -state with an exchange integral of the order of 1100 cm$^{-1}$ is formed [11–13]. Nano-granular Pt (C) consists of fcc-Pt crystallites of 1.5–5 nm diameter embedded in an amorphous carbon matrix. Pt(C) grown by FEBID has shown to provide a model system for studying charge transport effects in nano-granular metals [15] with tunable inter-grain coupling strength [16, 17]. In a nano-granular metal charge transport occurs via inelastic tunneling between the metallic grains. Due to the very small size of the individual Pt crystallites, this charge transport is governed by the charging energy $E_C$ associated with each tunnel event. It is this charging energy which is very sensitive to the dielectric properties of neighboring dielectric layers. As a consequence, the onset of the FE state associated with a strong increase of the dielectric constant $\varepsilon_r(T)$ of TTF-CA can be detected as a very pronounced change in the temperature-dependent conductance of the nano-granular metal. Because of the FEBID fabrication method
of the nano-granular metal, our approach provides excellent down-scaling capabilities. Monitoring the FE state on the lateral scale down to the limit defined by FEBID, i.e. 20–30 nm for nanostructures with electrical contact leads, can therefore be envisioned.

2. Experimental methods

Nano-granular microstrip structures were prepared by FEBID using the precursor Me3CpMePt (IV) (Cp: cyclopentadienyl, Me: methyl) at 5 kV beam voltage and 1.6 nA beam current on n-doped Si(100)/ SiO2 (200 nm) and pre-patterned Cr/Au electrodes. Under these preparation conditions the Pt metal content amounted to about 22 at%, as deduced from *in situ* energy dispersive x-ray analysis. The inter-granular tunnel coupling strength $g$ was increased by post-growth electron irradiation with a dose of 100 nC $\mu$m$^{-2}$, as detailed in [18]. By this the room-temperature conductivity increased from about $16 \Omega^{-1}$ m$^{-1}$ for the as-grown sample to $2 \times 10^3 \Omega^{-1}$ m$^{-1}$ after irradiation.

TTF-CA thin film growth was accomplished by molecular beam deposition at a base pressure of $5 \times 10^{-7}$ mbar using single-source evaporation of stoichiometrically mixed proportions of TTF and CA (Alfa Aesar, purity $\geq 97\%$, as supplied) at 366 K effusion cell temperature from a quartz liner. The growth rate was set to 0.8 nm s$^{-1}$ for a typical layer thickness of 50 nm. In several preparatory experiments we found the sticking coefficients of TTF and CA at room temperature to be extremely low. Stable thin film growth conditions at low growth rates were achieved at 193 K substrate temperature with liquid nitrogen cooling. For
reference purposes thick-film growth at several 10 nm−1 growth rate was performed on substrates with interdigitized electrode structures. In x-ray diffraction experiments (Bruker MRD, parallel beam optics, Cu-Kα) we found for both, thick and thin films, non-textured, polycrystalline layer formation on the amorphous substrate surfaces. By atomic force microscopy in air (non-contact mode, Nanosurf Easyscan 2) we found island growth (see figure 2).

Temperature-dependent conductance data were taken at constant bias voltage (Keithley sourcemeters 2400 and 2636A) in a 4He variable temperature insert. For thick TTF-CA film the bias voltage was set to 10 V (3 × 10⁴ V cm⁻¹) in order to get sufficiently large currents (see figure 1). Dielectric measurements on these films were also performed at 10 V and 111 Hz employing an HP 4284A LCR meter (see inset of figure 1). Conductance measurements on the Pt(C) microstrips with 50 nm TTF-CA layers were taken at 100 V cm⁻¹ to a maximum of 1000 V cm⁻¹. The measurements were performed in two-probe geometry. However, we analyzed transfer resistance contributions by complementary three- and four-probe measurements on similar EBID structures over the accessible temperature range and found them to be smaller than 2%.

3. Results

For several micron thick TTF-CA reference layers on interdigitized electrodes the onset of the FE state can be seen by the associated conductance anomaly of TTF-CA itself (figure 1). In parallel, we monitored the dielectric susceptibility of TTF-CA by the capacitance change of the interdigitized electrodes in the vicinity of the phase transition (inset to figure 1). As in bulk crystals the phase transition occurs at 81 K and is accompanied by a strong increase of the
conductance and capacitance. However, for thin films to exhibit clamping effects, layer thicknesses below about 100 nm are necessary. For these direct conductance measurements proved to be impossible, as even for thick films the resistance rapidly increases to several ten GΩ just below the phase transition. More importantly, the additional charge carriers injected into the FE will disturb the charge carrier dynamics intrinsic to the FE itself [20]. Here we follow a different approach. In a two-layer heterostructure of a nano-granular Pt(C) microstrip (see inset to figure 2) with a 50 nm TTF-CA top layer the application of a voltage between the electrodes leads to an electric field acting in parallel along the nano-granular metal and the organic FE. Due to the very large resistance of the organic thin film the current flow is restricted to the Pt(C) microstrip. The pronounced increase of the dielectric constant of TTF-CA at the PE–FE phase transition now strongly modulates the charge transport in the nano-granular metal. In figure 3 we show the conductance versus temperature behavior of three Pt(C) microstrips with different thicknesses. Each of the microstrips is covered with a 50 nm thick polycrystalline layer of TTF-CA. For reference purposes we also include conductance data obtained on two analogous Pt(C) microstrips without TTF-CA coverage. We note: (1) in contrast to the pronounced thermally activated behavior of the conductance of uncovered Pt(C), for TTF-CA covered Pt(C) the reduction of the conductance is much weaker as the temperature is reduced. (2) The Pt(C) microstrips show a pronounced increase of the apparent conductance noise in the temperature range 50 K to 65 K (100 nm sample) and 50 K to 56 K (20 nm sample),

Figure 3. Temperature-dependent conductance data of Pt(C) microstrips of different thickness with TTF-CA top layer. \(d\) denotes the respective doses used in a post-growth electron irradiation step for \(g\) tuning (see [17] for details). The associated conductance increase of the Pt(C) microstrips by post-growth irradiation becomes apparent by comparison with the reference curve (blue dashed line). The data is normalized to the respective conductance value of the Pt(C) microstrips at 95 K for clarity. The dashed lines (red and blue) represent the results obtained on uncovered Pt(C) microstrips. The dotted lines show the data for TTF-CA-covered Pt(C) microstrips as measured, whereas the solid lines are obtained from a running average over 20 data points.
respectively. For the 100 nm thick microstrip the noisy data follow a peak-like feature. This becomes also apparent for the 20 nm microstrip after applying a running average. The noise onset for the 20 nm sample coincides with the peak observed for the 100 nm sample. (3) For the 10 nm microstrip the overall temperature dependence of the conductance, albeit still thermally activated, is very weak. No peak is observed in the measured temperature range.

From these observations we conclude: (a) the peak-like anomalies between 50 K and 65 K are the consequence of a strong reduction of the charging energy $E_C$ in the nano-granular material caused by the PE–FE transition in the TTF-CA top layer. (b) The rather large dielectric constant $\varepsilon_r \approx 500$ of TTF-CA along the $a$-axis [21], even out of the immediate PE–FE phase transition region, leads to a reduced charging energy which results in an overall weakened thermally activated transport behavior. We assume here a predominant $a$-axis orientation of the TTF-CA top layer islands which results in a strong suppression of the thermally activated conductance behavior. For typical values of $\varepsilon_r^{(a)}$ up to and larger than 500 at the PE–FE transition [21] the charging energy renormalization becomes saturated over a wide temperature range, so that no clear peak structure at the phase transition occurs. (c) A different shape of the dielectric anomaly in TTF-CA at the phase transition caused by dielectric anisotropy [21] may be the reason why the peak shapes of the conductance of the 20 nm and 100 nm microstrip are different. We associate this to the random crystallographic orientations of the majority of the TTF-CA growth domains on top of the respective Pt(C) microstrips. Next we present a rationale for these conclusions.

4. Discussion

Within the weak inter-grain coupling regime of relevance here, the dominant transport mechanism in nano-granular metals is a variable-range type hopping which takes Coulomb interactions into account [15]. In more detail, as an electron tunnel event between neighboring grains occurs an associated charging energy $E_C = e^2/2C$ ($C$: capacitance of a grain in the effective surrounding nano-granular medium) has to be overcome. As the temperature is reduced correlated tunneling of more than one electron can occur and sequential inelastic cotunneling becomes the dominating transport channel. This leads to the following conductivity versus temperature behavior [15]

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/2}], \quad k_B T_0 \approx e^2/4\pi\varepsilon_0\varepsilon_r \xi(T), \quad (1)$$

whereby a weakly temperature-dependent attenuation length $\xi(T)$ of the electronic wave function is introduced. The activation temperature $T_0$ depends on two accounts on the dielectric constant experienced by the embedded metallic grain. First, $T_0$ is inversely proportional to the effective dielectric constant $\varepsilon_r$ of the matrix in which the grain is embedded. Second, $\xi$ depends also on the effective dielectric constant by way of its dependence on the charging energy [15]

$$\xi(T) = 2D/\ln \left( E_C^2/16\pi g(k_B T)^2 \right), \quad (2)$$

where $D$ denotes the grain diameter. For a spherical grain the capacitance is $C = 2\pi\varepsilon_0\varepsilon_r D$, so that $E_C$ is also inversely proportional to $\varepsilon_r$.

We now apply a model that contains the essential aspects for describing the observed conductance anomalies of the Pt(C) microstrips with a dielectric top layer on a mean-field level
The model describes the change of the effective dielectric constant experienced by the metallic grains at various distances to the Pt(C)/TTF-CA interface. Very briefly, the Coulomb potential at a given point \( r \) created by a point charge at position \( r' \) in the second layer of the trilayer structure (substrate/Pt(C)/TTF-CA) is calculated (see schematic in figure 4). This can be accomplished by an repeated image charge method leading to an expression for the Coulomb potential \( e/4\pi\varepsilon_0\varepsilon_r(r)r \). In a second step, the capacitance of a sphere in the second layer is obtained by the source point collocation method which uses the fact that the surface of a metallic sphere is an equipotential surface. For details of this model calculation we refer to [19].

In the inset to figure 4 we show exemplary results for the charging energy \( E_C(z) = e^2/2C(z) \) as a function of the distance \( z \) from the Pt(C)/TTF-CA interface assuming different dielectric constants for the TTF-CA layer, as indicated. Two trends are apparent. First, the strongest renormalization effects due to the proximity to the high-dielectric layer occur within a near-interface region of about 20 nm. Second, for \( \varepsilon_r^{\text{TTF-CA}} \) larger than about 100 the renormalization saturates. We now use the results for \( C(z) = 2\pi\varepsilon_0\varepsilon_r(z)D \) to calculate the expected qualitative temperature dependence of the conductance of the Pt(C) microstrips. For this we rely on a simplified parallel-circuit model for the nano-granular metal. We assume that it

\[\text{Figure 4. Result of model calculation of the temperature-dependent conductance of a nano-granular metal within a three-layer structure (see schematic). The temperature dependence of the dielectric constant of the TTF-CA top layer in the two main axis directions} \ a \ \text{and} \ c’-\text{axis is assumed to follow a Lorentzian with a half-width at half maximum of} \ 2 \ \text{K and peak values of} \ 500 \ \text{and} \ 50, \ \text{respectively. The dashed line indicates} \ T_C \ \text{which is set to} \ 56 \ \text{K. Blue line:} \ \text{Pt(C) thickness} \ t = 20 \ \text{nm, Pt grain diameter} \ D = 1.5 \ \text{nm,} \ g = 0.01. \ \text{Green line:} \ \text{Pt(C) thickness} \ t = 20 \ \text{nm,} \ D = 3.0 \ \text{nm,} \ g = 0.1. \ \text{Red line:} \ t = 10 \ \text{nm,} \ D = 3.0 \ \text{nm,} \ g = 0.1. \ \text{The dashed line represents the calculated Pt(C) conductance without TTF-CA top layer. Inset:} \ E_C \ \text{for spherical Pt particle with} D = 3 \ \text{nm diameter at different positions below the TTF-CA top layer, as indicated. The different curves were calculated for different} \ varepsilon_r^{\text{TTF-CA}} \ \text{as indicated. For all simulations the dielectric constant of the Pt(C) layer as effective medium was set to} \ 5.0 \ \text{and for SiO}_2 \ \text{it was set to} \ 2.8.\]
consists of equidistant layers of regularly arranged spheres of equal diameter $D$. We use the respective $z$-dependent values of the capacitance and dielectric constant to obtain the respective layer conductances $\{\sigma_i(T; z_i)\}$ and obtain the overall conductance by summation: $\sigma(T) = \sum_i \sigma_i(T; z_i)$. In figure 4 the results are shown for a 10 nm and a 20 nm thick nano-granular metal layer assuming different orientations of the TTF-CA top layer, as indicated. For the 20 nm thick nano-granular metal we find a peak-like anomaly in the temperature-dependent conductance at the PE–FE phase transition of the TTF-CA top layer at 56 K, if we assume that TTF-CA has its stacking axis in-plane, as in the $c^*$-orientation (blue curve in figure 4). For the temperature-dependent dielectric constant of the TTF-CA top layer along the $c^*$-direction we use a Lorentzian shape. If we assume $a$-axis orientation of the TTF-CA layer with a correspondingly larger dielectric constant of 500 at $T_C$, an overall increase of the temperature-dependent conductance of the nano-granular metal results but no peak structure. This is due to the saturation effect in the renormalization of the charging energy for $\varepsilon_{\text{TTF-CA}}$ larger than about 100. This same behavior occurs assuming a 10 nm thick nano-granular metal layer. Here we show in figure 4 (red curve) the result of a model calculation assuming $a$-axis orientation of the TTF-CA top layer with a maximum of the dielectric constant of 500 at $T_C$. An overall damping of the thermally activated behavior and no peak structure result. We finish the modeling by showing the influence of an increased inter-granular coupling strength $g$. For the 20 nm thick nano-granular metal the green curve in figure 4 shows the conductance behavior for $g = 0.1$ with TTF-CA being in the $c^*$-orientation. Assuming two different inter-granular coupling strength, namely $g = 0.01$ and $g = 0.1$, we can rather well reproduce the experimentally observed conductance anomalies for the 20 nm and 100 nm layer in figure 3. In conjunction with the two different $g$-values, representing the as-grown (100 nm) and post-growth electron irradiated Pt(C) layer (20 nm), we assume an increase of the grain diameter from 1.5 nm to 3.0 nm, as this is experimentally observed [18]. Further comparing the simulated conductance behavior with the experimental results we conclude that for the 20 nm and 100 nm thick Pt(C) microstrips the TTF-CA top layers are at least partly formed by growth domains with their stacking axis in-plane (such as in $c^*$-orientation) which leads to a conductance peak at $T_C$, whereas for the 10 nm Pt(C) microstrip the TTF-CA growth domains have mostly $a$-axis orientation and thus only show an overall enhanced conductance in the whole temperature range. We cannot back this reasoning by independent structural evidence for the suggested orientations of the TTF-CA growth domains on the particular Pt(C) microstrips of different thickness, since this would require a structure-sensitive probe that can operate on the lateral size of the growth domains of about 500 nm. However, we consider the amorphous structure of the carbonaceous matrix of the nano-granular metal at the interface to the organic FE layer and the amorphous SiO$_2$ surface to be equivalent templates for polycrystalline TTF-CA islands growths (see figure 2). We conclude this part by noting that a rather small set of TTF-CA growth domains is covering the Pt(C) microstrip, so that the conductance modulations are not subject to a pronounced averaging effect. We therefore believe that the $E_C$ renormalization will likely acquire a time dependence which stems from charge fluctuations in the TTF-CA FE domains as the domain walls move by thermal activation [20]. Also, if an extended PE–FE coexistence region, known to occur in bulk crystals [22], is also present in the clamped TTF-CA layers, any time-dependence in the spatial arrangement of the PE and FE phase volumes will be reflected in the nano-granular metals’ conductance. We therefore argue that the Pt(C) microstrips also represent a probe of the time-dependent dielectric properties of the FE (and PE) layer.
We note that this parallel circuit model is highly simplifying, since it is only directly applicable for diffusive charge transport. Here, due to the disordered nature of the Pt(C) nano-granular layer, a tunnel-percolative transport that minimizes the overall electrostatic energy may be assumed [23]. However, so far no theory was developed that would take both, the percolative nature and the correlated co-tunneling scenario into account. We assume that the effect of charging energy renormalization due to the TTF-CA layer will be qualitatively well described by our approach as long as the thickness of the nano-granular metal layer does not significantly exceed the screening length of about 20 nm in the present case. We also want to point out that a possible small parallel conductance contribution directly through the highly resistive TTF-CA layer can be efficiently suppressed by fine-tuning the Pt(C) conductance to a higher value by a small degree of irradiation, as was done here. We performed analogous experiments on as-grown samples and found the same qualitative conductance modulation effects caused by the TTF-CA layer. Here we focused on the results with briefly irradiated Pt(C) microstrips for two additional reasons. First, the intrinsic current noise under fixed bias voltage conditions of as-grown Pt(C) samples is higher than for samples briefly irradiated with 100 nC μm−2. For these the low-temperature transport of nano-granular Pt(C) is still of the correlated variable-range hopping type but the resistivity is reduced by more than two orders of magnitude. Second, as-grown Pt(C) samples show a time-dependence of their resistance (aging effect) which can be very efficiently cured by the brief irradiation treatment.

An important observation from our experiments is that the apparent phase transition temperature is shifted by 25 K from 81 K to about 56 K. We attribute this to clamping. From the known temperature-dependent thermal expansion coefficient of Si (bulk of substrate material) [24] and TTF-CA [25] we calculate the thermally-induced clamping strain assuming full clamping as the heterostructure is cooled from the growth temperature (193 K) to 81 K. Depending on the orientation of the respective TTF-CA growth domain this leads to strain values of 0.2% to 1.0%, with the larger strain value referring to the stack axis lying in the substrate plane. The associated stress values can only be estimated from the bulk modulus of TTF-CA [26], since no measurements of the temperature-dependent elastic constants of TTF-CA are known to us. From this we estimate stress levels of 14 MPa to 69 MPa. The hydrostatic pressure dependence of $T_C$ obtained for single crystals [27] shows an almost linear pressure dependence of $dT_C/dP = 0.34$ K MPa$^{-1}$ in the relevant temperature range from 80 K to about 200 K. If we use this tentatively for the biaxially clamped TTF-CA thin layers under tensile strain we expect a $T_C$ shift of 5 K to 23 K, with the large value for the $c^*$-axis orientation. This analysis is hindered by the non-availability of reference data for the anisotropic elastic constants of TTF-CA and the lack of independent data concerning the influence of biaxial strain on the phase transition temperature. Nevertheless, in conjunction with the model calculation that suggests a predominant $c^*$-axis orientation, i.e. in-plane polarization, for the samples which exhibit a pronounced peak at 56 K in the Pt(C) conductance data, our estimate of the $T_C$ shift of 23 K is amazingly close to the observed shift. We therefore suppose that it is the clamping effect that is responsible for the reduced $T_C$ and would consider possible size effects not to be important, because the in-plane orientation of the stacking axis should lead to to very small depolarization effects.
5. Conclusion

In this work we suggest a size-scalable heterostructure consisting of a nano-granular metal and a FE layer in which the nano-granular metal acts as a sensitive and non-invasive probe of the (time-dependent) dielectric properties of the FE layer. As a consequence of the fabrication technique for the nano-granular metal, FEBID, the probing structure can be scaled-down to the size of a single growth domain of the FE layer. With proper design of the probing structure this does also allow for studying the spatial distribution of the dielectric properties. Based on the writing capabilities of FEBID and the typical grain size of 1.5 nm to 5 nm for the nano-granular metal, we expect similar performance of the probing structure as described here down to probing areas of 20 nm to 30 nm. We have shown this probing effect for the organic FE TTF-CA as a case study and found, as an additional important observation, that clamping can be very efficient in tuning the phase transition temperature for TTF-CA. However, our approach should also be applicable to inorganic FEs and, in particular, also for a reversed order of the layer structure with the nano-granular metal deposited on the top of a pre-formed, and possibly epitaxial, FE layer. We conclude by remarking on the observed saturation effect in the charging energy renormalization for dielectric constants significantly above 100. In this case, an even more sensitive probe structure can be envisioned, consisting of a dense array of isolated metallic nano-dot structures between which the FE (or any other dielectric material) is filled-in as matrix material. Recent theoretical work predicts strong conductance renormalization effects in this case [28, 29]. Experimental work along these lines is in progress.

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