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# Electrical transport and magnetic properties of metal/metal oxide/metal junctions based on anodized metal oxides

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**Abstract:** In this paper we present magnetoelectric properties of metal/metal-oxide/metal junctions. We use Ti and Fe as metallic layers separated by the porous metal-oxides of iron or titanium formed with the anodization method. This allowed to prepare double junctions with at least one ferromagnetic layer. Here we show magnetoresistance and current-voltage characteristics of the junctions together with their magnetic characteristics. We found positive or negative magnetoresistance depending on junction composition. We discuss also the nature of differential resistance calculated from  $I$ - $V$  characteristics. Our findings show that the strongest influence on observed behaviour has a top metallic layer and the interface between this layer and anodized oxide where strong interatomic diffusion is expected.

**Keywords:** magnetic junction; magnetoelectric properties; metal-oxides; porous; anodization, thin film

## 1. Introduction

A large concern for metal-oxides came from their compelling physical properties such as magnetic and electrical [1,2]. For example, growing attention is observed for magnetic semiconductors, *i.e.* diluted semiconductors like doped titanium oxides [3,4] and not-diluted semiconductors like hematite [5], also the magnetic half-metals, such as magnetite, experience large interest [6]. For instance, the junctions composed of the titanium- and iron-based metal oxides being the main purpose of this study are widely considered for electronics and spintronics [7,8]. The semiconducting metal oxide/metal heterostructures can form a junction with the Schottky barrier [9] or if the magnetic oxide is used it can induce spin-polarization of the charge carriers, an effect found in semiconducting hematite [10], insulating maghemite [11] and half-metallic magnetite [12]. Furthermore, the wide bandgap metallic oxide semiconductors have a bandgap above 2 eV and show the ability to work at elevated temperatures, high frequencies and high powers [13].

Additionally, the patterned semiconducting oxide layers are interesting as a potential material for photoelectrochemical and photocatalytic purposes [14], as demonstrated in the case of titanium oxide with a bandgap of  $\sim 3.0 - 3.2$  eV [15]. The nanotubular anodized titanium oxide was shown to form a Schottky barrier between Ti and  $\text{TiO}_2$  and the importance of structural defects on semiconducting properties was also discussed [16,17]. The impact of defects especially in non-stoichiometric  $\text{TiO}_2$  can lead to the  $n$ - (oxygen deficient) or  $p$ -type (titanium deficient) semiconductor [18]. Defects can also induce weak ferromagnetism in paramagnetic titanium oxides, as observed for anatase, rutile and  $\text{TiO}$  rock salts [19–21].

The iron oxides show a large variety of magnetic and transport properties. The magnetite has an inverse spinel structure and is ferrimagnetic half-metal that changes into insulator below the Verwey transition ( $\sim 125$  K) [22]. In contrary the hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) is a semiconductor with a bandgap of 2.0 eV [23]. It is antiferromagnetic below Néel temperature of 950 K and undergoes the Morin transition at 260 K between easy-axis and easy-plane antiferromagnet with small canting between sublattices resulting from Dzyaloshinskii–Moriya interaction [24]. In turn, maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) is

ferrimagnet with magnetite-like inverse spinel structure and hematite-like stoichiometry, for which the charge neutrality is obtained because of the presence of Fe ions vacancies [25]. The hematite ([26]) and magnetite ([27]) have demonstrated their applicability in oxide-based junctions with the Schottky barrier.

Electrochemical anodization, used in this work for the formation of oxide layers, is a well-known technique. It allows the oxidation of metals as well as the preparation of porous and patterned structures [28]. Furthermore, it is a relatively easy and low-cost method that can be applied to large sample areas and complex surfaces. A great variety of compounds are successfully anodized, including titanium [29] and iron [30], for which anodized titanium oxide (ATiO) and anodized iron oxide (AFeO) are created at the metal surface. The as-anodized oxides have an amorphous structure or exhibit poor crystallinity. The transformation of as-anodized oxide into a well defined crystallographic structure can be performed by annealing at elevated temperatures. The anodized oxides after the annealing at around 773 K are efficiently transformed into a mixture of oxides with dominant rutile phase for ATiO [31] and hematite for AFeO [32].

The anodized layers are often used for the preparation of nanopatterned structures for catalytics, photovoltaics, plasmonic or biomedical materials [33–36], and as templates for patterned thin films [37,38] or nanowires [39]. Here we exhibit an innovative idea to use the anodization process for the preparation of metal-oxide based junctions. We show results of magnetoelectric studies of junctions formed with Fe, Ti and their oxides for which the properties strongly depend on the junctions compositions. We observed a strong influence of top metallic layer, either ferromagnetic iron or paramagnetic titanium. For the case of ferromagnetic top metallic layer the magnetoelectric effect is strong and dominates the transport properties. On the other hand, for the top paramagnetic layer the semiconducting properties of the oxides become dominant and govern the electrical transport of the junction.

## 2. Materials and Methods

We prepared metal/anodized metal oxide/metal junctions with different compositions as listed in Table 1. First, we deposited a metallic multilayer stack consisting of 50 nm of titanium adhesive layer followed by 100 nm of gold layer for electrical contact and a 300 nm layer of titanium or iron on 17 mm × 17 mm Si(001) substrate. The deposition was performed at room temperature with e-gun evaporation system (ESV4, Leybold GmbH, Cologne, Germany) in a vacuum chamber at the pressure of  $10^{-5}$  mbar. The thickness of the films was controlled with the quartz detector. The 300 nm of Ti or Fe was deposited through round mask with a diameter of 10 mm positioned at the centre of the substrate. The ATiO or AFeO oxide layers were formed using the anodization method. Approximately half of the titanium or iron layer thickness was oxidized. Next the samples were covered with 50 nm of titanium or iron and 50 nm of gold. The top gold layer provides electric contact and protection against contamination from the atmosphere. The deposition of the last metallic and gold layers was done through a cylindrical mask with a diameter of 7 mm positioned at the centre of the samples. The intention of successive reduction of the planar size of deposited layers was the prevention of short-circuiting at the edges between the layers.

**Table 1.** List of samples.

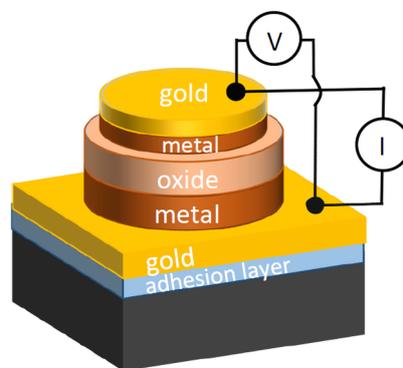
Sample labeling	Si/Ti adhesion layer/bottom Au electrical contact/ <b>junction</b> /top Au electrical contact
<b>FAF</b>	Si/Ti <sub>50nm</sub> /Au <sub>100nm</sub> / <b>Fe/AFeO/Fe</b> <sub>50nm</sub> /Au <sub>50nm</sub>
<b>FAT</b>	Si/Ti <sub>50nm</sub> /Au <sub>100nm</sub> / <b>Fe/AFeO/Ti</b> <sub>50nm</sub> /Au <sub>50nm</sub>
<b>TAF</b>	Si/Ti <sub>50nm</sub> /Au <sub>100nm</sub> / <b>Ti/ATiO/Fe</b> <sub>50nm</sub> /Au <sub>50nm</sub>

The anodization was performed with a homemade two-electrode system with the platinum cathode and the metallic layer used as an anode (for more details see [40]). The parameters of anodization were the same for all samples ensuring the formation of the porous oxide layers with

similar thicknesses. The anodization was performed at room temperature for 45 minutes at a constant anodizing voltage of 5 V. The electrolyte composed of 0.3 wt.%  $\text{NH}_4\text{F}$  + 1 wt. %  $\text{H}_2\text{O}$  dissolved in  $\text{C}_3\text{H}_8\text{O}_3$  was used. The last step of samples preparation was a thermal annealing at 747 K performed for 60 minutes in a vacuum chamber to improve the structural properties of ATiO and AFeO layers.

X-ray diffraction (XRD) measurements were executed with Panalytical XPert Pro diffractometer (Almelo, Netherlands) equipped with Cu lamp working at 40 kV and 30 mA using  $K_{\alpha 1}$  wavelength. The Bragg-Brentano geometry was adopted and each sample was measured in  $2\theta$  range of 20 – 90 degrees. Details about the measurement protocol and equipment setup used in our laboratory can be found in [41]. Morphology studies were performed with a scanning electron microscope (SEM, Tescan Vega 3, Fuveau, France) with a secondary electron detector. Magnetic properties were measured with MPMS SQUID XL magnetometer (Quantum Design, San Diego, CA, USA) on samples of approximately 3 mm  $\times$  3 mm size. The measurements were done in magnetic fields between  $\pm 50$  kOe applied in a parallel and perpendicular direction to the sample surface ( $H\parallel I$  and  $H\perp I$ ) and for a temperature range between 10 K and 300 K. The magnetization values were normalized with respect to the total volume of the deposited material.

The studies of electrical transport properties were performed with standard four-probe technique and involved magnetoresistance ( $MR$ ) and current-voltage characteristic ( $I$ - $V$ ) measurements. A sketch of the junction is presented in Figure 1. The electrical contacts are assembled to the bottom and top gold layers and the measurement is done through the metal/metal oxide/metal junction. We used Keithley 2400 current source, Keithley 2182A nanovoltmeter, and channel switcher Keithley 3706A (Tektronix Company, Beaverton, OR, USA) during the measurements. The control of temperature and magnetic field was provided by the SQUID XL magnetometer. The  $MR$  and  $I$ - $V$  studies were conducted in a field range of  $\pm 50$  kOe at high (300 K) and low (5 K) temperatures in longitudinal and transverse geometries, *i.e.*  $H\parallel I$  ( $H\perp S$ ) and  $H\perp I$  ( $H\perp S$ ), respectively.



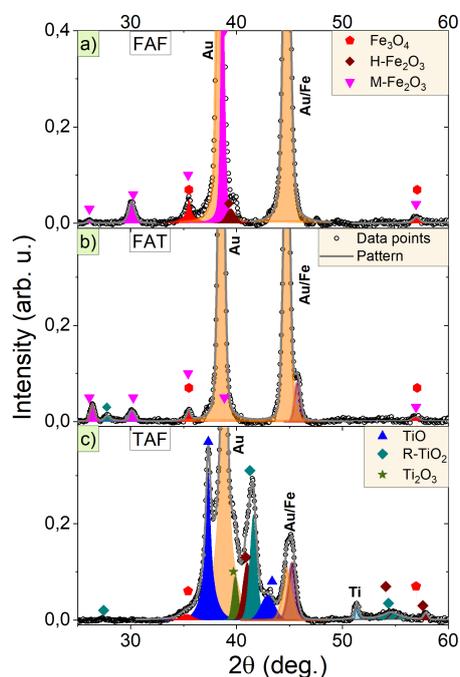
**Figure 1.** Schematic view of the metal/metal-oxide/metal junction.

### 3. Results and Discussion

#### 3.1. XRD studies

Diffraction patterns of FAF, FAT and TAF junctions are presented in Figure 2. The peaks of constituent layers of Au, Ti, Fe as well as iron and titanium oxides are identified. The strongest signal is from the gold layers. The peak at 38.2 degrees from Au (111) crystallographic plane with maximal intensity is observed in all junctions showing preferential growth in this crystallographic direction, *i.e.* the most densely packed direction of  $fcc$  structure. The most intense diffraction peaks from titanium and iron layers have similar positions as gold and they are strongly overlapped. The presence of  $bcc$  Fe phase [42] is well noticeable at approximately 45 degrees. We observed that the intensity of common Au/Fe peak decreases in dependence on iron content in the junction. The Ti which typically crystallizes in  $hcp$  structure was identified only in the diffractogram of TAF junction but it is known that

for thin films a stable Ti *fcc* phase can be also found with a lattice constant of  $a = 4.05 \text{ \AA}$  [43,44], very close to the lattice constant of Au  $a = 4.07 \text{ \AA}$  [45]. Hence the identification of this phase in presented diffractograms is practically impossible.



**Figure 2.** XRD patterns for a) FAF, b) FAT, c) TAF metal/metal oxide/metal junctions. The titanium and iron oxides are marked with different tags corresponding to different metal oxides.

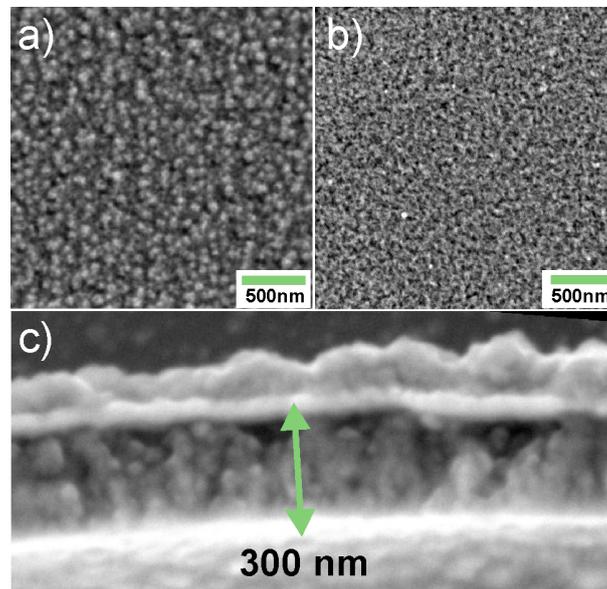
It is seen that AFeO is a mixture of hematite, magnetite and maghemite in FAF, while only magnetite and maghemite were observed for FAT junctions. The ATiO layer of TAF junction shows a signal from rutile, TiO and  $\text{Ti}_2\text{O}_3$  while no anatase phase was found. In most cases, the anatase is a precursor of rutile formation and for bulk the transformation of anatase into the rutile takes place at temperatures of 873 K or higher [31], about 100 degrees more than in our studies. The lack of anatase phase suggests good efficiency of used annealing process which enabled the formation of a more stable rutile phase. The reduction of transformation temperature with the size of nanostructures was already observed by Bauer *et al.* [46].

Furthermore, in TAF sample the diffraction maxima that can be related to hematite and magnetite are found. A similar but less pronounced situation is observed for FAT junction where a signal from the rutile was observed. Such behaviour indicates material intermixing and diffusion at the interface of anodized oxide and the top metallic layer. The interatomic diffusion happens during annealing process and results in partial oxidation of metallic layer. Such diffusion may also induce the formation of ternary iron titanates phases ([47]), but we have not identified appropriate diffraction maxima. The expected subtle changes in the cell parameters caused by small admixtures and small peak intensities were not observed.

### 3.2. SEM imaging

Figure 3 presents SEM images of the surface of ATiO and AFeO metal oxides directly after the anodization and annealing. The presented images were collected from the part of the sample surfaces not covered with metals, as shown in Figure 1. The morphology of titanium and iron oxide layers has a porous form with some differences in grain dimensions. The size of grains observed on the ATiO surface is larger, between 75 – 100 nm, while for AFeO the grains are smaller (50 nm or less). For anodized oxide layers covered with metal the porous pattern is replicated on the metallic surface. The Figure 3 c presents an exemplary cross-section of the AFeO layer. The thickness of the oxide formed

after 45 minutes of anodization was found to be about 300 nm while the thickness of the remaining bottom metallic layer is estimated to be 150 nm, basing on anodization current *vs.* time curves. In case of anodization process the thickness of the oxide layer increases significantly as compared to consumed metal thickness. This process is governed by the ratio of cell volume of oxide and cell volume of metal, but also depends on anodization conditions [29].

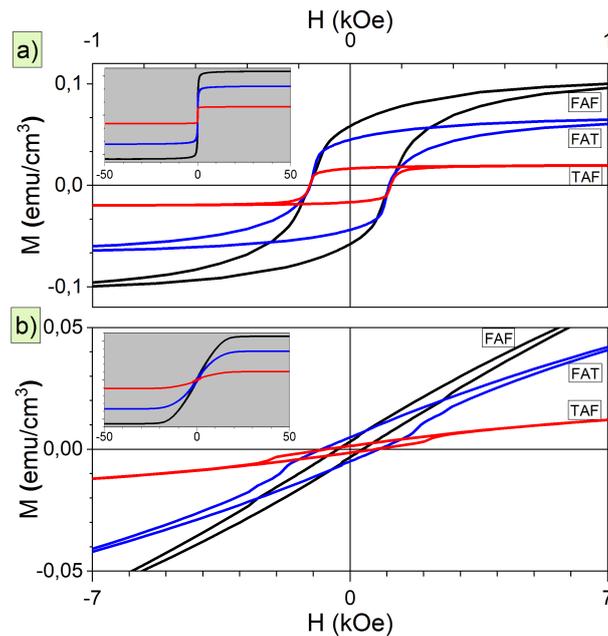


**Figure 3.** SEM images of a) anodized titanium oxide layer and b) anodized iron oxide layer. The bottom image c shows a cross-section of AFeO.

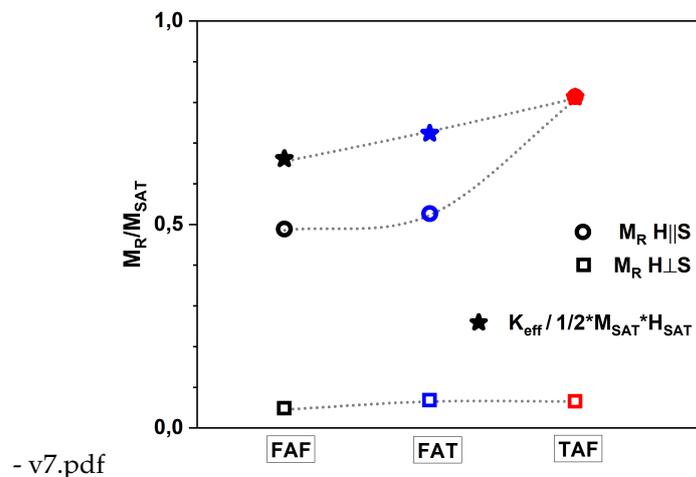
### 3.3. Magnetic properties

The magnitude of the magnetic signal strongly depends on the composition of the bottom and top metallic layers and anodized oxide layer; more iron atoms in the sample induce higher net magnetization. Figure 4 presents the results of field-dependent magnetization curves collected at room temperature for the magnetic field applied in  $H\parallel S$  and  $H\perp S$  directions. The insets show the results of  $M(H)$  dependencies in full range of magnetic field. The shape of the hysteresis curves indicate that an easy magnetic direction lies in the plane.

The values of magnetic remanence normalized to the saturation magnetization ( $M_R/M_{SAT}$ ) for both geometries are presented in Figure 5. The remanence values for  $H\perp S$  direction are below 0.1 while for  $H\parallel S$  geometry are around 0.5 for FAF and FAT and 0.8 for TAF junctions. Such values show strong influence of shape anisotropy associated with in-plane easy magnetic direction. We calculated, based on the approach presented in [48], the effective magnetic anisotropy constant ( $K_{eff}$ ) to confirm the role of shape anisotropy. The estimation of the magnetic anisotropy degree was done by calculating the ratio  $K_{eff}/(1/2M_{SAT}H_{SAT})$  with  $M_{SAT}$  and  $H_{SAT}$  being the saturation magnetization and magnetic field for hard magnetic direction. Such ratio will be equal to 1 for a case of ideal magnetic anisotropy and 0 for isotropic distribution of magnetic moments. The obtained values are between 0.65 – 0.85 and confirm the presence of strong non-perfect in-plane magnetic anisotropy reflected also in opened curves for  $H\perp S$  direction and their slanted shape for  $H\parallel S$  direction. Surprisingly the strongest magnetic anisotropy and remanence were found for TAF junction with only one ferromagnetic layer and smaller content of iron than for FAF junction.



**Figure 4.** Field dependent magnetization curves for FAF, FAT and TAF junctions measured at room temperature for a)  $H\parallel S$  and b)  $H\perp S$  geometry. The insets show the  $M(H)$  curves in the range of a magnetic field of  $\pm 50$  kOe.

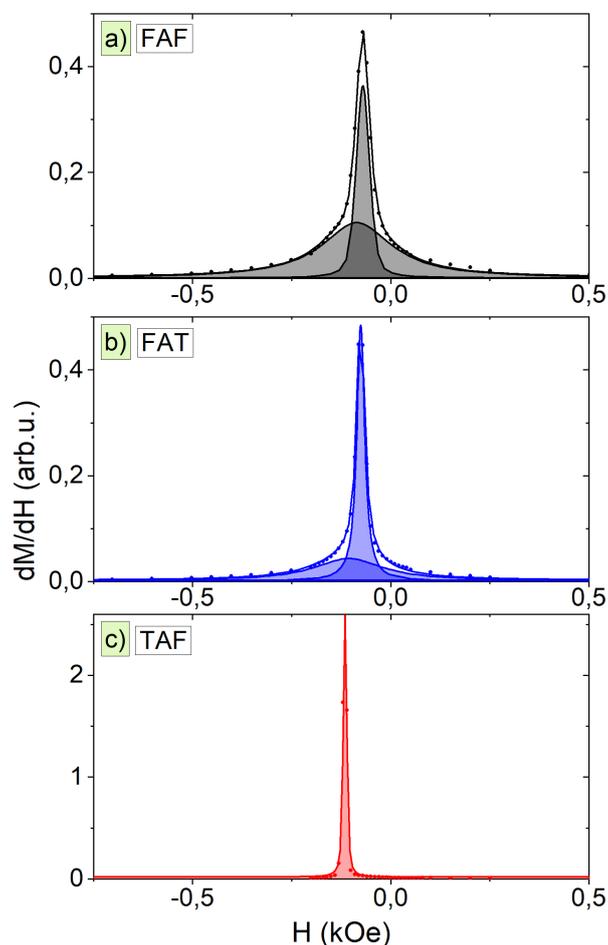


**Figure 5.** Normalized remanence magnetization ( $M_R/M_{SAT}$ ) values for  $H\parallel S$  and  $H\perp S$  directions and normalized anisotropy constant calculated for FAF, FAT and TAF junctions at room temperature.

The hysteresis curves were also used to evaluate the switching field  $H_{SF}$  and its distribution. The switching field, defined as the field at which the inflexion on the  $M(H)$  curve occurs corresponding to the situation when a maximal number of magnetic moments changes orientation for opposite, has been calculated as a maximum of  $M(H)$  derivative. We have quantified also the *FWHM* of switching field distribution *SFD* and percentage contributions of the magnetic components. The *SFD* informs about the magnetic homogeneity of the sample: if the magnetic moments alter the direction simultaneously the *SFD* is narrow, but if the switching is scattered for a wider range of magnetic fields the distribution of the switching field is large. Such *SFD* broadening can be observed for grains or clusters of magnetic material with different sizes or for chemically disordered samples. The results of the  $H_{SF}$  distribution at 300 K for  $H\parallel S$  geometry are shown in Figure 6. The presence of two switching field components indicates the existence of two distinct magnetic contributions. These components have similar values of the mean switching field but differ in *SFD* widths; one is narrow and the other is broad. The

exception is TAF junction for which we found only one component with a narrow distribution. The existence of two magnetic components in FAF and FAT junctions can be explained as follows: one component with narrow distribution comes from iron layers, while the other with broad distribution originates from chemically disordered AFeO layer consisting different phases of iron oxides as was previously demonstrated by XRD studies.

The values of  $H_{SF}$ ,  $SFD$  and coercive field ( $H_C$ ) obtained at 10 K and 300 K for the magnetic field applied for easy and hard magnetic direction are collected in Table A1 of Appendix. We observed a weak influence of temperature and the similar values of  $H_{SF}$  and  $H_C$  for  $H\parallel S$ , while for hard magnetic direction the switching field is several times larger than the coercivity. The distribution of switching fields for  $H\perp S$  geometry is very broad reflecting the influence of magnetic anisotropy. In this case, the  $SFD$  for the main component has 15 – 20 kOe and is comparable with  $H_{SAT}$  (see Figure 4 b). The remaining part of the magnetic signal that accounts for a few or several percentages for  $H\perp S$  geometry corresponds to the strongly pinned magnetic moments that are responsible for open hysteresis curves and non-zero coercivity. The pinning effect can appear at the interface between metallic film and oxide layer in this porous system.



**Figure 6.** A magnetization derivative of hysteresis curves for a) FAF, b) FAT, and c) TAF junctions measured at 300 K for  $H\parallel S$  geometry.

### 3.4. Electrical transport properties

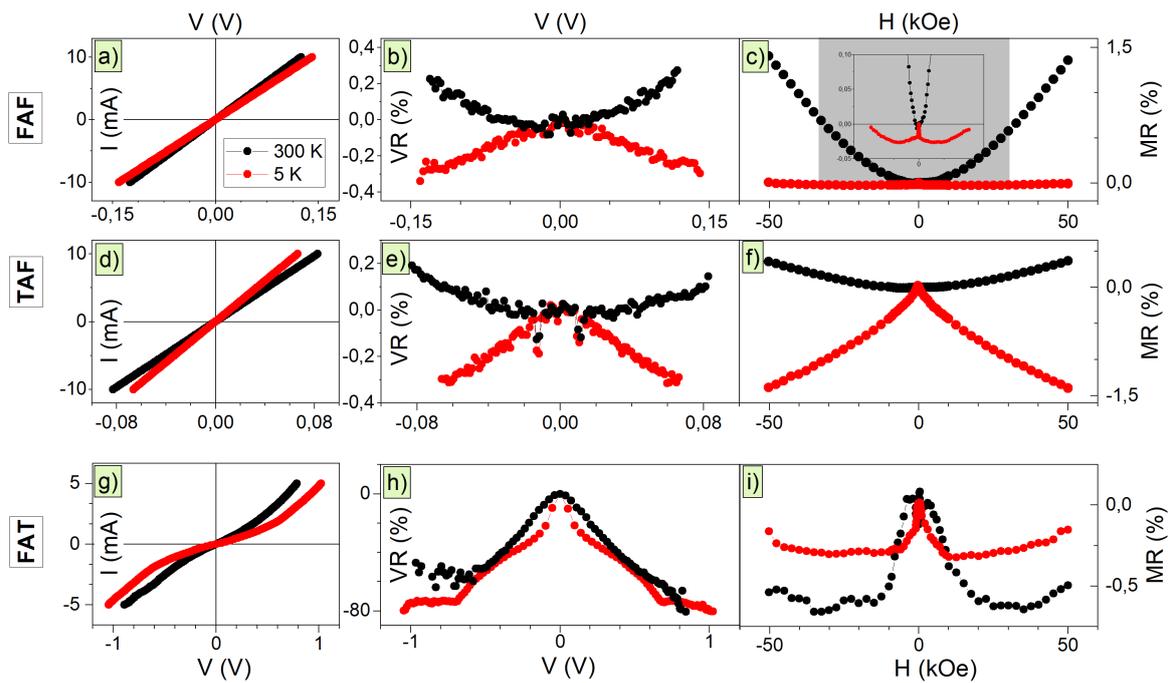
The current-voltage characteristics ( $I$ - $V$ ) and magnetoresistance dependencies ( $MR = \frac{R(H) - R(H=0)}{R(H=0)}$ ) of junctions were measured at 5 K and 300 K. Figure 7 presents results for longitudinal configuration since the measurement geometry does not affect the obtained results. The  $I$ - $V$

characteristics presented in Figure 7 for FAF and TAF samples, *i.e.* junctions terminated with iron demonstrate the ohmic type of conductivity. The characteristics are symmetric as a function of polarization voltage and the rectifying ratio, *i.e.* the ratio of forward to reverse current at maximal voltage, is equal to 1 with accuracy better than  $\pm 1\%$ . In contrary the FAT junction has a strongly nonlinear  $I$ - $V$  characteristic (see Figure 7 g). For the bipolar junction of semiconducting metal-oxide with a double Schottky diode the nonlinear, but symmetric with polarization voltage current-voltage dependence is usually observed, as found for FAT sample. The rectifying ratio in this case is slightly above 1.1 at 300 K and reduces to 1.02 at 5 K. The shape of the  $I$ - $V$  curve for FAT junction is characteristic for varistor of a two-terminal bipolar diode, where  $I = R(V)^\alpha * V$  [49,50] with  $\alpha$  being the nonlinearity coefficient. The stronger variation of  $\alpha$  from unity the stronger deviation from ohmic-type of conductivity. The obtained value of the nonlinearity coefficient  $\alpha = \frac{R}{R_{diff}} = \frac{(V/I)}{(dI/dV)^{-1}}$  [51] in case of FAT junction is around 1.5(1) at 300 K and increases to 2.0(1) at 5 K and does not show variation with magnetic field or measurements geometry. The switching voltage between passive and active state, *i.e.* a voltage for which a strong deviation from linear  $I$ - $V$  dependence occurs, is around 0.6 V. Similar values of nonlinearity coefficient and switching voltage were found for iron titanites, such as mixtures of hematite-ilmenite with semiconducting properties [50,52]. Therefore it can be expected that the varistor-like properties in FAT sample might be a result of the intermixing and formation of Fe-Ti-O oxide barrier at the interface between AFeO and top Ti layer. The effect of atomic intermixing in our junctions was previously identified in XRD studies. The values of the nonlinearity factor are relatively small as compared with the most effective varistors based on ZnO or SnO<sub>2</sub> ceramics where it can reach values of several dozen or above hundred [53,54]. However in these materials, the switching voltage is very large and the active state is obtained for gating with several or more volts, an order of magnitude more than in case of FAT junction.

After careful analysis of the nonlinearity coefficient  $\alpha$  and in particular the differential resistance  $R_{diff}(V) = (\frac{dI}{dV})^{-1}$  (calculated from  $I$ - $V$  characteristics) a presence of weak deviation from linearity and hence from ohmic conductivity has been found in all junctions. Results of normalized values of voltage-dependent differential resistance, the  $VR = \frac{R_{diff}(V) - R_{diff}(V=0)}{R_{diff}(V=0)}$ , are presented in Figure 7 together with determined magnetoresistance values  $MR$ .

The comparison of  $MR$  and  $VR$  dependencies shows a distinct differences between samples. The junctions with Fe as a top layer (FAF and TAF) show strong  $MR$  and weak  $VR$  effects while FAT sample exhibits opposite trend. This suggests that the transport properties are governed by the properties of the top metallic layer and the interface between this top layer and anodized oxide. For iron used as the top layer the influence of the magnetic field on transport properties is strong and the magnetoresistance effect is large. In contrary, for the 'non-magnetic' titanium layer the influence of the electric field becomes more evident and the semiconducting properties of the oxide govern the conducting of the junction and induce a presence of a Schottky-like barrier.

Furthermore, the FAF and TAF junctions show the change of sign for  $MR$  and  $VR$  parameters from positive to negative with lowering the temperature. At room temperature both parameters have positive values while at low temperatures they become negative. The negative values of  $VR$  seen in Figure 7 are the artefact resulting from normalization procedure and no negative differential resistance was obtained in our samples. The positive value of magnetoresistance is a result of Lorentz force acting on electrons leading to a parabolic shape of  $MR$  known as ordinary magnetoresistance of metals. At low temperature the negative anisotropic  $MR$  is strong in TAF sample and dominates for the whole range of magnetic fields, while for FAF sample it is weaker and turns into positive parabolic dependence after reaching magnetic saturation. Additionally, in both junctions, a lack or a weak dependence of measurements geometry on  $MR$  and  $VR$  was found. The  $VR$  response is very weak with a similar magnitude at low and high temperature. This suggests that the electric barrier formed at the interface between the iron layer and both anodized oxides shows a weak semiconducting character.



**Figure 7.**  $I$ - $V$  characteristics (a, d, g) with changes of differential resistivity induced with voltage  $VR(V)$  (b, e, h) and magnetoresistance  $MR(H)$  (c, f, i) for FAF, TAF, and FAT junctions. Inset of figure 7 c is a magnification of FAF magnetoresistance dependence.

The negative  $VR$  and  $MR$  dependencies in FAT are demonstrated in Figure 7 h and i, respectively. The  $VR$  reaches  $-80\%$  while the  $MR$  is  $-0.5\%$ . The  $VR$  dependence becomes flat for voltage larger than  $\pm 0.6$  V, *i.e.* when the switching voltage for varistor is achieved. The  $MR$  demonstrates the parabolic-like nature in the range of magnetic field of 0 and  $\pm 15$  kOe, and for larger field its value becomes independent of magnetic field. The value of  $\sim 15$  kOe is comparable with the saturation field found in magnetization studies suggesting that the change in behaviour of magnetoresistivity is connected with reorientation and alignment of magnetic moments in the AFeO and bottom Fe layer of the junction. The negative value of  $MR$  can result from the presence of giant magnetoresistance ( $GMR$ ) of granular samples or domain wall resistance ( $DWR$ ). The  $DWR$  arising from a scattering of charge carriers at the boundaries of the magnetic domains was previously identified in iron [55,56], while the presence of  $GMR$  was found in magnetite nanoparticles [57] and explained as a gradual relative alignment of magnetic moments between neighbouring particles. The anisotropic magnetoresistance effect ( $AMR$ ) is another possibility for explaining the appearance of negative  $MR$ . In  $AMR$  a strong dependence of relative direction of current and magnetization vector on the resistivity value is expected [58]. In this case, the magnetoresistance should show a change of sign from positive for longitudinal to negative for transverse geometry, an effect not present in our samples. The effect of  $MR$  sign change was previously observed in iron thin films [59]. A small reduction of  $MR$  amplitude for different measurement geometry found in FAT sample could indicate that the  $AMR$  might be present in this junction but its importance is minor. Therefore all three effects, the  $GMR$ ,  $DWR$  and  $AMR$  can contribute to the observed total negative  $MR$  effect, but they cannot be unambiguously identified.

Additionally, we measured the  $MR(T)$  curves of FAF and TAF junctions to better understand processes related to sign changes of magnetoresistance. Figure 8 shows temperature dependent resistivity collected without and with magnetic field of 10 kOe and determined values of  $MR$ . The temperatures at which  $MR$  changes sign are marked with red lines in Figure 8. The change of  $MR$  sign was found at 43(1) K for FAF and at 213(1) K for TAF samples.

The effect of magnetoresistance inversion with temperature was previously reported for magnetite thin film and iron epitaxial thin films by Yoon and Hong [60] and Granberg *et al* [59], respectively. In

magnetite film the inversion was observed at 264 K. This temperature is higher than our findings for TAF and FAF junction, but since the magnetite phase was found in all our samples we can assume that its presence can be responsible for observed *MR* behaviour. Yoon and Hong attributed the phenomena of *MR* sign reversing to the *DWR* effect and the scattering of electrons leading to their temperature-dependent spin-flip inside the domain wall. This effect increases the spin diffusion length and decreases the domain wall width with lowering temperature. Such behaviour can lead to the change of *MR* sign at transition temperature [61]. In case of porous samples prepared with the anodization process we observed a mixture of oxides which induce phase homogeneity and chemical disorder. A diffusion length can be strongly reduced by these factors leading to the decrease of the transition temperature.

Granberg *et al.*, on the other hand, considered two distinct contributions to the change of magnetoresistance sign with temperature for longitudinal geometry in Fe(001) single crystal thin film. The first negative contribution comes from Lorentz force acting on conduction carriers in ferromagnet. The second component, the extraordinary *MR* effect, arises from spin-orbit coupling and strongly depends on the relative direction of the external magnetic field and the direction of the current within the single magnetic domain which brought a positive *MR* for single crystalline iron. Therefore, the observed magnetoresistance of Fe thin film is an effect of the competition of ordinary and extraordinary effects. If the temperature is changed the scattering length of both components change in a different way leading to an *MR* sign inversion. Granberg *et al.* determine the temperature of *MR* sign reversal being approximately 70 K which is close to FAF junction inversion temperature. Additionally, he observed also strong dependence of inversion temperature on measurement geometry and film thickness. His result showed that only in samples with a thickness larger than  $\sim 30$  nm the *MR* sign change with temperature is observed from positive to negative values if measured in longitudinal geometry, in contrary to the sample measured in transverse geometry with negative to positive *MR* sign change. In our case of polycrystalline porous samples, the *MR* exhibits no measurement geometry dependence indicating that the scattering at the grain boundaries or interface of oxide and top metal layer is dominant.

#### 4. Conclusions

In this paper, we showed that the electrochemical anodization process can be used as an easy way for oxidation of metallic layers and formation of magnetic metal/porous oxide junctions. We have studied iron and titanium compounds and prepared metal/metal oxide/metal junctions with different combination of elements. The anodization conditions, like time and voltage, were chosen in such a way that we oxidize approximately half of the metal layer creating 300 nm thick porous oxide layer. The XRD analysis allowed us to identify various phases of metallic oxides confirming strong inhomogeneity of the samples. The atomic intermixing at the interface between oxide and metallic layer has been observed, an effect well pronounced for mixed TAF or FAT junctions where magnetite and hematite or rutile were found, respectively. The chemical inhomogeneities and structural defects influence the magnetic and electrical transport properties. In particular, a large switching field distribution and non-uniform magnetization reversal mechanism were found. Detailed analysis of differential resistivity proven a presence of non-linear current-voltage dependence. The FAT junction showed strong negative *VR*, independently on the geometry and temperature of measurements. Also, the *MR* for this sample had only negative values. In contrary, for FAF and TAF junctions we observed the presence of change of *VR* sign from positive to negative with lowering temperature. Similar behaviour was found for magnetoresistance for which we observed the competition between ordinary *MR* and combination of *DWR*, *GMR* or *AMR* phenomena. This competition led to the temperature dependent change of *MR* sign: at high *T* the *MR* sign was positive while at low *T* a negative value was observed. The mutual correlation of the *VR* and *MR* signs indicates that the scattering of the charge carriers and hence the magnetic or electric field dependence of conductivity properties have the same origin, related to the energy barrier at the metal/oxide interface, porous structure and chemical inhomogeneity of

the samples. The important aspect of this study is the influence of the top metallic layer, whether it is a ferromagnetic iron or paramagnetic titanium, and the barrier formed at the interface between this layer and the oxide.

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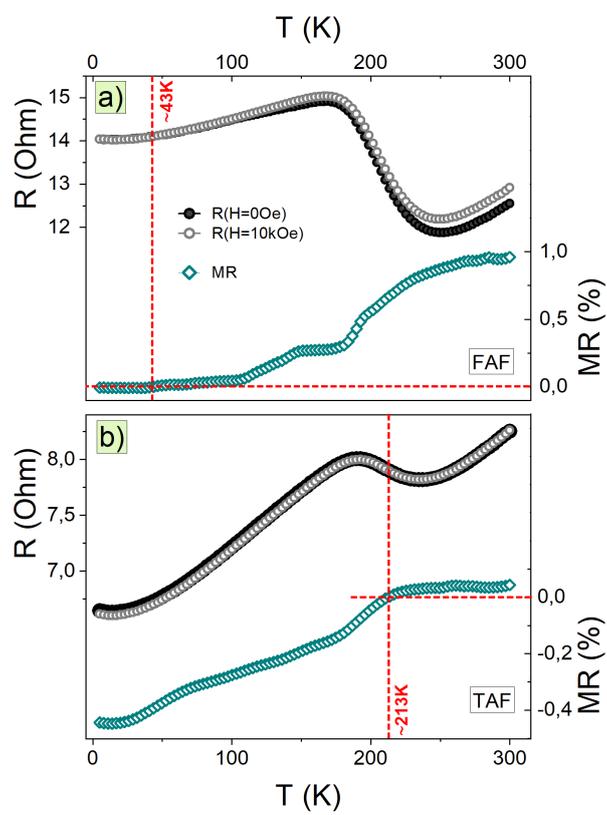
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## Appendix A

**Table A1.** Values of coercive field ( $H_C$ ), switching field ( $H_{SF}$ ) and its width and percentage area for  $H\parallel S$  and  $H\perp S$  measured at low and high temperature.

$H\parallel S$ geometry	10 K				300 K			
	$H_C$ (kOe)	Area (%)	$H_{SF}$ (kOe)	Width (kOe)	$H_C$ (kOe)	Area (%)	$H_{SF}$ (kOe)	Width (kOe)
<b>FAF</b>	0.16(1)	32(1)	0.15(1)	0.13(1)	0.07(1)	34(1)	0.07(1)	0.04(1)
		68(1)	0.15(1)	0.69(1)		66(1)	0.09(1)	0.21(1)
<b>TAF</b>	0.16(1)	58(1)	0.14(1)	0.03(1)	0.08(1)	56(1)	0.08(1)	0.02(1)
		42(1)	0.21(1)	0.16(1)		44(1)	0.11(1)	0.22(1)
<b>FAT</b>	0.16(1)	100	0.16(1)	0.03(1)	0.12(1)	100	0.128(1)	0.0(1)
$H\perp S$ geometry	10 K				300 K			
	$H_C$ (kOe)	Area (%)	$H_{SF}$ (kOe)	Width (kOe)	$H_C$ (kOe)	Area (%)	$H_{SF}$ (kOe)	Width (kOe)
<b>FAF</b>	0.33(1)	99(1)	~ 0	24.25(4)	0.44(1)	95(1)	~ 0	22.25(2)
		1(1)	0.46(1)	2.56(4)		5(1)	0.70(1)	1.33(2)
<b>TAF</b>	0.79(1)	92(1)	~ 0	23.45(5)	0.65(1)	91(1)	~ 0	22.39(4)
		3(1)	1.82(1)	0.29(1)		9(1)	0.96(1)	0.67(1)
<b>FAT</b>	0.68(1)	85	~ 0	26.11(3)	0.82(1)	94(1)	~ 0	25.58(1)
		6(1)	2.17(1)	0.51(1)		6(1)	1.17(1)	0.04(1)
		9(1)	0.11(1)	5.53(1)				



**Figure 8.** Temperature dependent resistivity  $R(T)$  measured without and with a magnetic field of 10 kOe and corresponding magnetoresistance values for **a)** FAF and **b)** TAF junctions.

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