

Electro-mechanical coupling of semiconductor film grown on stainless steel by oxidation

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(Received 14 June 2013; accepted 18 September 2013; published online 3 October 2013)

Electro-mechanical coupling phenomenon in oxidation film on stainless steel has been discovered by using current-sensing atomic force microscopy, along with the I-V curves measurements. The oxidation films exhibit either ohmic, *n*-type, or *p*-type semiconductor properties, according to the obtained I-V curves. This technique allows characterizing oxidation films with high spatial resolution. Semiconductor properties of oxidation films must be considered as additional stress corrosion cracking mechanisms. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4824072>]

It is generally known that stainless steel (SS) has good corrosion resistance due to protective passive film formation.^{1–3} However, SS resistance to stress corrosion cracking (SCC) is poor, especially in chloride-containing environments.⁴ The SCC resistance is largely affected by the structure, thickness, and composition of the passive film.⁵ Slip dissolution model is commonly used to describe the SCC mechanism. According to the slip dissolution model, stress-induced film mechanical rupture is the key and prerequisite condition leading to SCC. However, this model only considers one aspect of SCC, which is the stress effect on film fracture. SCC is an electrochemical process, thus the passive film composition, for example, Fe₂O₃, Cr₂O₃, FeOOH, NiO, etc., which exhibit different semiconductor properties,^{2,5,6} is also thought to control the SCC behavior.^{7–10} The effects of externally applied stress on the film semiconductor properties have not been previously discussed in the literature.

Current sensing AFM (CSAFM) is a technique to map the current between the conductive tip and the surface with nanometer spatial resolution.^{1,11} CSAFM can acquire the electrical conductivity of the passive film by measuring the current at a given applied voltage, along with obtaining local current-voltage (I-V) curves. Moreover, the force between the tip and the sample surface can be adjusted. Thus, CSAFM is regarded as an effective tool to investigate the externally applied stress effects on the film semiconductor properties.

Oxides, like Cr₂O₃ and NiO, behave as the *p*-type semiconductors, which are the result of metal ion or cation deficiency.¹² However, Fe₂O₃ and FeOOH behave as the *n*-type semiconductors, which are the result of oxygen vacancies and metal interstitials.¹³ The composition of SS passive or oxidation films, which are a mixture of diverse oxides of Fe, Cr, Ni, Mo, mixed Fe-Cr oxides, etc., along with the corresponding defects, contribute to the resulting *p*-type and *n*-type film properties.¹⁴

Mott-Schottky analysis using electrochemical impedance spectroscopy (EIS) and photo-electrochemical methods

have been widely used to identify semiconductor characteristics of passive films on stainless steel.^{15–18} However, these are relatively macroscopic measuring methods, meaning that some micro-inhomogeneities are not accounted for. Also, the EIS test is conducted in solution and the results depend on the frequency^{19,20} and the applied potential.²¹ This paper introduces a method to measure passive film semiconducting properties with high spatial resolution.

The materials used are 2507 duplex SS (DSS) and 316L austenitic SS (ASS) single crystals. The specimens were first wet ground with SiC paper up to 2000 grit. The 2507 DSS specimen was then mechanically polished with diamond paste to 1.5 μm. Both specimens were also electrochemically polished to eliminate surface stress. The detailed polishing conditions for the 2507 DSS are: 50 vol. % HNO₃ solution at the 1.2 V potential for 30 s at 25 °C. For the 316L ASS, the solution was H₃PO₄ 650 ml/l, H₂SO₄ 250 ml/l, CrO₃ 80 g/l, ethylene glycol 10 g/l, with 20 V potential held for 60 s at 70 °C. The samples were ultrasonically cleaned in ethanol after electrochemical polishing. Indentations were then made on the sample surfaces with digital micro-hardness tester, HVS-1000, to mark the same scanning region. The 2507 DSS sample was held in air at room temperature (RT), which is about 25 °C for 24 h to form stable oxidation film and then placed in the resistance furnace at 300 °C for 30 min to obtain thicker and denser oxidation film layer. However, the 316L ASS samples were placed in the resistance furnace at 300 °C and 400 °C for 30 min, respectively, to form the oxidation films.

The CSAFM schematic is shown in Fig. 1(a). The probes used were DPE14/AIBS, coated with Pt. The nominal tip radius was less than 50 nm with 5.7 N/m force constant. CSAFM uses contact AFM with a voltage bias applied to the tip, while scanning the sample surface, so the current or film conductivity map along with the topography map can be obtained simultaneously. Local I-V curves can be also obtained by placing the tip at a fixed position. Obtained local I-V curves in Fig. 1(b) present three characteristics: linear, almost symmetric, and asymmetric. In addition, almost symmetric and asymmetric I-V curves present high resistance in one polarity and much lower resistance in the opposite polarity, same as in the literature results.¹

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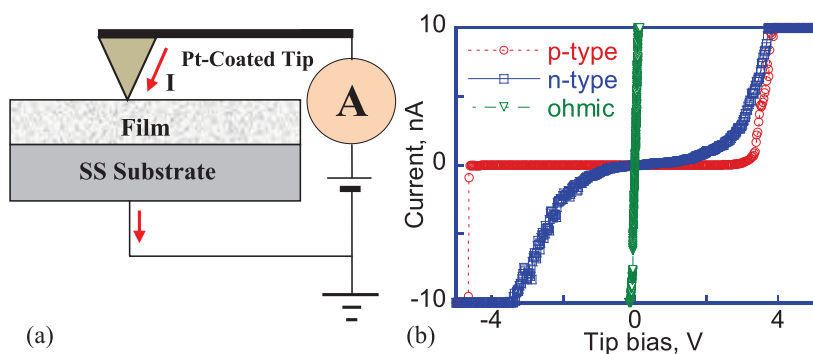


FIG. 1. (a) CSAFM measurement schematics, illustrating a MSM structure; (b) three types of experimentally measured I-V curves: ohmic, p-type, and n-type.

Based on the schematic in Fig. 1(a), metal-semiconductor-metal (MSM) structure is formed, as two metal-semiconductor contacts are present, between the tip and the film, and between the film and the SS substrate. The metal-semiconductor contact can be either a Schottky junction or an ohmic contact, depending on the relative values of the metal and the semiconductor work functions, and on the semiconductor type. Schottky junctions are formed when the metal work function is higher than that of the *n*-type semiconductor or smaller than that of the *p*-type semiconductor, according to the Fermi levels ad-equation. In this case, for the *n*-type semiconductor, the flow of electrons from the semiconductor to the metal was prevented with the positive applied voltage and a substantial electron flow from the semiconductor to the metal was enhanced with the negative applied voltage. For the *p*-type semiconductor, similar arguments can be applied. Thus, if measured almost symmetric or asymmetric I-V curve has higher resistance with positive applied voltage, the semiconductor is regarded as the *n*-type, and, oppositely, if it has higher resistance with negative applied voltage, then the semiconductor is thought to be the *p*-type. In another case, when the work function of the metal is smaller than that of the *n*-type semiconductor, or greater than that of the *p*-type semiconductor, ohmic contacts are formed,²² reflected by linear I-V curves.

Thus, in the MSM structure, if the measured I-V curve is linear, the two metal-semiconductor contacts are both expected to be ohmic. If the I-V curve is almost symmetric, then one contact is ohmic and the other one is the Schottky junction. When two contacts are both Schottky junctions, the I-V curve is asymmetric. Three types of I-V curves were experimentally observed: asymmetric *p*-type, almost symmetric *n*-type, and linear (ohmic), seen in Fig. 1(b). These three I-V curves were acquired from the 2507 DSS oxidation film formed at 300 °C (*p*-type), 316L oxidation film formed at 400 °C (*n*-type), and the oxidation film formed at 300 °C (ohmic).

In CSAFM, the force between the tip and the sample can be calculated as Force = Deflection × Sensitivity × Spring constant, where the spring constant depends on the probes used (5.7 N/m here) and the sensitivity was obtained from the force-distance curves (32 nm/V, experimentally measured). Deflection could be adjusted by changing the setpoint value during imaging. In this experiment, a normal force of 328 nN was needed to obtain clear images, since CSAFM uses contact mode AFM.

MFM measurements were performed to distinguish austenite and ferrite. AES depth profiles were obtained to estimate the thickness of the oxidation film. The thickness of the

oxidation film was thought to be the depth profile at which the oxygen concentration has dropped to half of its value at the surface.²³

Figures 2(a) and 2(b) show the MFM and topography maps of the 2507 DSS specimen after oxidation films formation in the same scan region. The MFM map allows distinguishing austenite and ferrite, since they are paramagnetic and ferromagnetic, respectively.²⁴ Austenite appears higher (brighter) than ferrite in topography maps, thus contact AFM topography maps can also be used to distinguish between austenite and ferrite.

Figures 2(c) and 2(d) show the 2507 DSS oxidation film formed at RT AFM and current images with 0.8 V applied tip bias. Oxidation film on austenite has better conductivity than on ferrite, also seen in Fig. 3(a). After oxidation at 300 °C, the current in both austenite and ferrite decreased significantly and became smaller than the 0.001 nA minimum measurable current with the same 0.8 V applied voltage, thus the current images are not shown here. By increasing the applied voltage to 7 V, the current increased, and the corresponding current map is shown in Fig. 2(e). Similar results are also seen in Fig. 3(a), where the current are smaller in both austenite and ferrite with the same applied tip bias after oxidation at 300 °C. Apparently, this is mainly attributed to the increased oxidation film thickness, and the thicknesses of oxidation films formed at RT and 300 °C were 4.6 nm and 18.4 nm, respectively, based on the AES measurements, shown in Figs. 3(c) and 3(d).

Additional 164 nN normal tip load largely increased the current in both austenite and ferrite, according to Fig. 2(f). The average current was 0.011 nA in austenite and 0.001 nA in ferrite initially. However, it increased to 9.91 nA in austenite and to 0.084 nA in ferrite after 164 nN additional tip normal load, according to current profiles in Figs. 2(e) and 2(f). As a result of the additional tip normal load, the current increased over 900 times in austenite and 80 times in ferrite. Moreover, the current in both austenite and ferrite returned back to the original values after additional force has been removed, same as in Fig. 2(e). This means that the film deformation was within the elastic range with the total tip normal load of 492 nN. Neglecting the adhesive force between the tip and the sample, Herizian elastic contact formula for a sphere on a flat can be used to calculate the contact area between the tip and the oxidation film, defined as in Refs. 25 and 26. The schematic is shown in Fig. 3(e)

$$A = \pi a^2 = \pi (3PR/4E^*)^{\frac{2}{3}}, \quad (1)$$

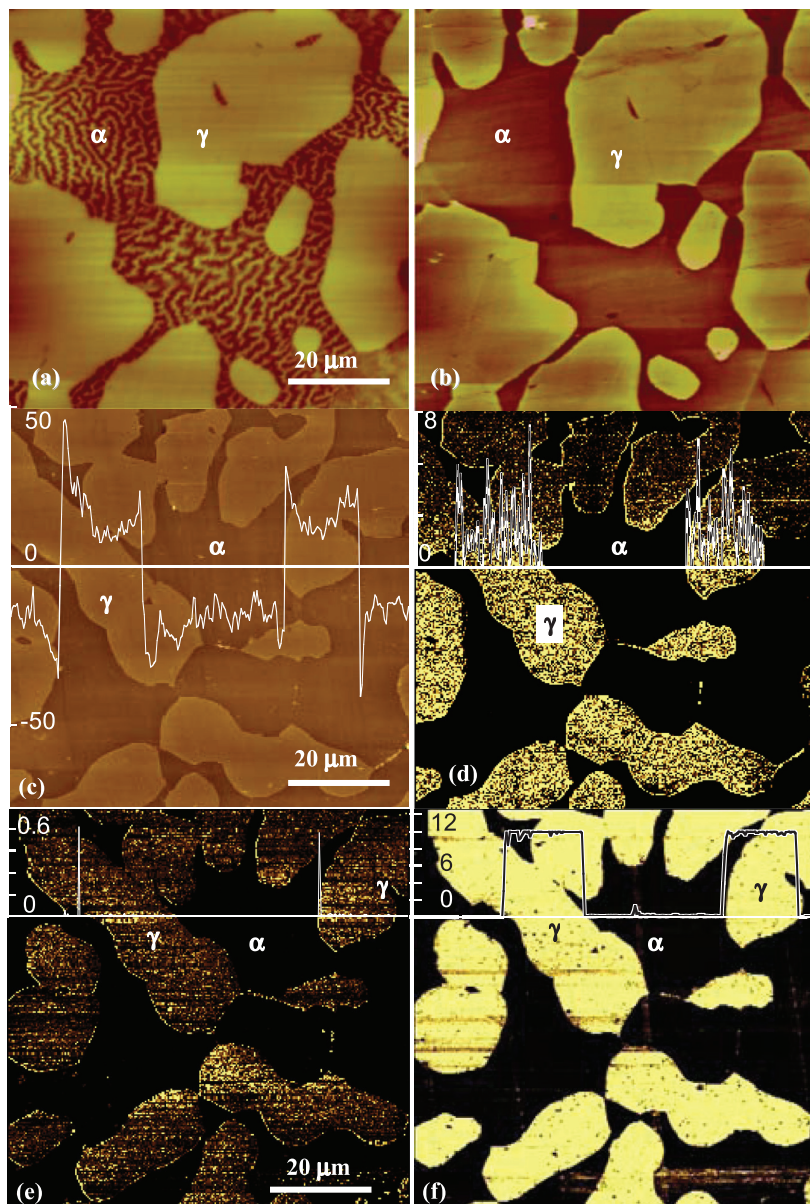


FIG. 2. (a) MFM image of the DSS after oxidation film formation; (b) AFM topography image of the same area as in (a). (c) AFM contact topography map of the DSS with the line height profile in nm; current maps with the line current profiles in nA of: (d) oxidation film formed at RT with 0.8 V tip bias and 328 nN tip normal load; (e) oxidation film formed at 300 °C for 30 min; (f) 7 V tip bias and 492 nN total tip normal load.

$$E^* = [(1 - \nu_1^2)/E_1 + (1 - \nu_2^2)/E_2]^{-1}. \quad (2)$$

Here, A is the contact area, a is the contact radius, E^* is the effective Young's modulus of the tip and the sample, P is the normal tip load, R is the tip radius. E_1 and E_2 , ν_1 and ν_2 are the Young's modulus and Poisson's ratios of the tip and the specimen. The following values were used for the tip: $E_1 = 169$ GPa, $\nu_1 = 0.28$ and the specimen: $E_2 = 200$ GPa, $\nu_2 = 0.3$.^{27,28} The current densities are then easily obtained by using the calculated contact area. The current densities were 1.42×10^8 nA/mm² in austenite and 1.29×10^7 nA/mm² in ferrite before additional normal tip and increased to 9.75×10^{10} nA/mm² in austenite and to 8.26×10^8 nA/mm² in ferrite after 164 nN additional tip normal load. Hence, the current density increased over 687 times in austenite and 64 times in ferrite, respectively, as discussed below.

Huge current increase after adding the normal force up to 492 nN was not a result of the oxidation film fracture, otherwise, the current would not return back to the original values after the additional force has been removed.

In addition, the decreased contact resistance between the tip and the sample as a result of increased normal tip load is not the main reason leading to such significant current increase. Fig. 3(b) shows a series of the linear I-V curves of 316L oxidation film formed at 300 °C under different loading force varied from 328 nN to 821 nN. In this case, the equivalent circuit is shown in Fig. 3(f). The slope reciprocals of the linear I-V curves could be regarded as the total resistance of the circuit. The total resistance, including contact resistance between the tip and the semiconductor film, R_{C1} , the resistances of the semiconductor film, R_S , the contact resistance between the film and the substrate, R_{C2} , and other resistances, R_r , such as the resistance of the substrate and the protective resistance of the measurement circuit (very low). The whole resistance decreased from 25.1 MΩ to 14.3 MΩ with the loading force increasing from 328 nN to 821 nN, calculated from the series of I-V curves in Fig. 3(b). R_{C1} and R_S were reduced at higher tip loading forces, owing to increased contact area between the tip and the film, along with decreased effective oxidation film thickness, since the tip

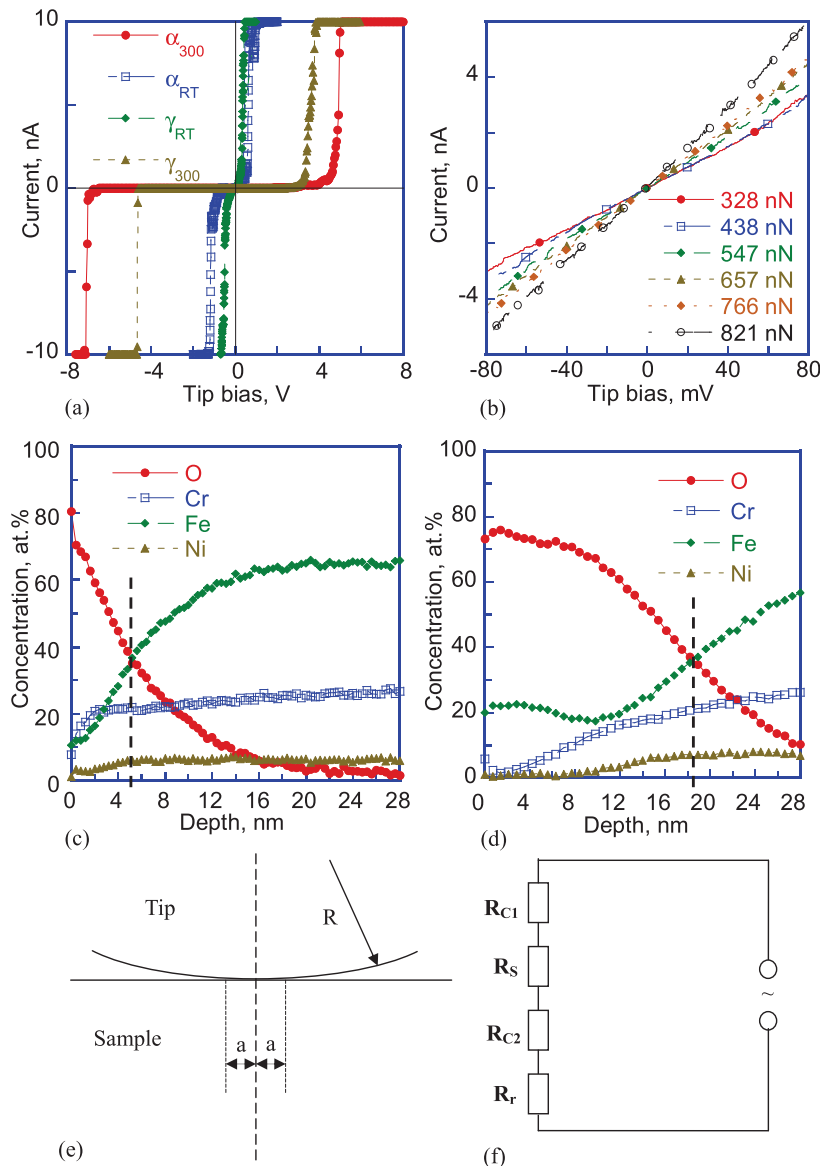


FIG. 3. (a) I-V curves of the DSS oxidation films formed at RT and 300 °C, respectively; (b) I-V curves of the 316L ASS oxidation film formed at 300 °C for 30 min with varying tip normal load. AES depth profiles (metallic cations and oxygen) of the DSS oxidation films: (c) formed at RT, (d) formed at 300 °C; (e) tip-sample contact model; (f) equivalent circuit of the CSAFM measurement.

elastically compressed the film. What's more, the calculated resistance is 20 M Ω when the normal tip force is 547 nN. Hence, one can assume that the contact resistance only decreased 1.25 times with the total 492 nN normal tip load applied to DSS oxidation film.

Thus, enormous current increase under greater compressive stress is possibly attributed to two mechanisms^{29,30} described below. One is the narrowed band gap effect, which results in giant carrier concentration growth for the same applied tip bias. The other appears to be related to more crystal defects due to larger compressive stress, and these defects give rise to intermediate tunneling levels.

Chromium is the major element used to form oxidation film and its corresponding oxides: mainly Cr₂O₃ in the oxidation film, regarded as compact oxide with low diffusion constants for oxygen and metals.³¹ This results in smaller current values and more uniform current distribution in ferrite, since ferrite contains more chromium, as seen in previous work.³² When considering that DSS oxidizes at 300 °C, many observations confirmed that differences existed in both the morphology and the film thickness between the two phases due to

different chemistries and crystal structure.^{33–35} This illustrates that the interface between the ferrite region and the oxide is flat, while on the austenite region it is more uneven, with many asperities present. Consequently, the oxidation film formed on the austenite region tends to be porous and nodular. Nevertheless, the oxidation film on the ferrite region is pore-free and homogeneous. What's more, the oxidation film formed on ferrite is slightly thicker than the film on austenite due to lower nickel content,³³ since nickel is an anti-oxidation element. Thus, the current density increased more in the oxidation film over austenite, attributed to porous morphology and relatively thinner oxidation film.

In conclusion, externally applied stress not only affects oxidation films mechanical properties, but also their semiconductor properties. So far mechanical film fracture due to externally applied stress, leading to SCC, has been the only reason considered. However, since the current increases significantly due to the film semiconductor properties variation with the applied stress and the environment, semiconductor properties must be accounted for when considering additional SCC mechanisms.

The authors acknowledge support from the National Natural Science Foundation of China (51161160563 and 51271026) and Beijing Municipal Commission of Education (YB20091000801). The authors acknowledge valuable discussions with Dr. Meng Li.

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