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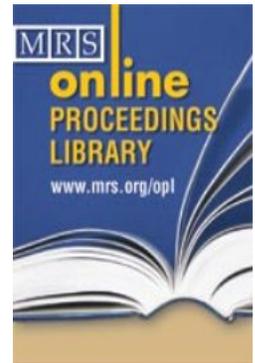
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## FLUCTUATION MICROSCOPY STUDIES OF ALUMINUM OXIDES EXPOSED TO CL IONS

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### Abstract

Fluctuation electron microscopy studies have been performed on several aluminum oxides exposed to different electrochemical conditions. Little is known about amorphous aluminum oxide structures and their relationship with their passivation behaviors. Corrosion studies have shown that exposure of aluminum oxide films to Cl ions in solution reduces the oxide's passivity, and this results in the onset of pitting corrosion. The physical changes that occur in the oxide as a result of Cl exposure have not been previously identified due to the difficulty in investigating the structure of this amorphous material. Fluctuation microscopy is a new electron microscopy technique that is able to detect the presence of medium range order structures in amorphous systems. In this paper, we will report fluctuation microscopy results on amorphous aluminum oxides that have been exposed to Cl ions in solution and compare them with oxides that have seen no electrolyte exposure or that have been exposed to electrolytes that do not contain Cl, such as  $\text{SO}_4^{2-}$  containing electrolytes. We will also compare the Cl-exposed oxides with oxides that have been implanted with Cl ions. The differences in pitting behaviors for these oxides are consistent with our previous speculation on the effect of medium range order on the passivation behavior of aluminum oxides grown using ozone.

### Introduction

Ultrathin films of aluminum oxide are important for a variety of solid state electronic devices, including superconducting Josephson junctions [1], single electron transistors [2], and magnetic tunnel junctions [3]. Thin aluminum oxide films passivate the surface of aluminum and provide resistance against corrosion [3]. Therefore, understanding of aluminum oxides structures is very desirable, as structures determine properties. There are however many open questions regarding amorphous aluminum oxides. Part of the reason is that it is hard to perform diffraction studies on those thin films. Even diffraction studies can only provide information on short-range order structures, which is not enough to describe amorphous structures.

Medium-range order is any structure order that falls into the range from 10 Å to 300 Å. There has been abundant evidence of the existence of such order. Until recently there have not been any experimental techniques that can directly characterize such structures quantitatively. However, medium-range structures do affect properties as we will show later this paper. In this paper, we apply fluctuation microscopy technique to directly measure medium range order

structures in several aluminum oxides exposed to different electrochemical conditions. We will report fluctuation microscopy results on amorphous aluminum oxides that have been exposed to Cl ions in solution and compare them with oxides that have seen no electrolyte exposure or that have been exposed to electrolytes that do not contain Cl<sup>-</sup>, such as SO<sub>4</sub><sup>2-</sup> containing electrolytes. We will also compare the Cl-exposed oxides with oxides that have been implanted with Cl ions.

## Experiments

Al oxide samples were fabricated by depositing about 200 nm of Al on 0.5 μm SiO<sub>2</sub> on Si followed by plasma-oxidation for 10 minutes in electron cyclotron resonance plasma. This produces a low defect density amorphous Al<sub>2</sub>O<sub>3</sub> layer on top of the Al layer. The thickness of this oxide is about 45 Å. These samples then went through four different processing conditions: 1) Sample A: as-grown sample; 2) Sample B: immersed in 0.05 M K<sub>2</sub>SO<sub>4</sub> for eight hours at open circuit; 3) Sample C: immersed in 0.05 M NaCl for eight hours at open circuit; 4) Sample D: anodically polarized to produce pitting in the Al in 0.05 M NaCl.

To prepare TEM specimens, the 45 Å oxide was scraped off the Al substrate with a razor blade into methanol solution and then dispersed in the solution using an ultrasonic cleaner. The methanol and oxide suspension was placed on a lacey carbon grid and air-dried.

To understand the short-range order in those films, we first took diffraction patterns and measured the reduced radial distribution function. The radial distribution function was extracted from diffraction patterns of the amorphous aluminum oxide. Small angle scattering was also cut off before Fourier transform was performed in order to remove the strong electron dynamical effect. This cut-off should not affect our results because small angle scattering does not contribute to the term that yields the radial distribution function. An edge smooth function was applied when the Fourier transform was performed. This procedure is to avoid artificial oscillations in the resultant radial distribution function. The RDF is an ensemble average of the short-range order structures (2 – 5 Å) of the whole sample. It cannot provide information on local structure changes at length scales larger than 5 Å, i.e., the medium-range order structures [4].

Fluctuation microscopy utilizes a phenomenon called speckle patterns. Although speckles have been found in all types of coherent imagery for many years [5], this microscopy technique is relatively new [6]. Speckle patterns are generated by interference under coherent scattering conditions. The intensity of each pixel in an image is actually contributed by electrons scattered by a small column from the sample. The volume of this column is determined by the resolution. Therefore, the intensity fluctuation is directly related to the local structure change in each small volume of the sample. By measuring the fluctuation of speckle intensity in a transmission electron microscope (TEM) dark-field image, atomic correlation beyond the two-body correlation can be extracted [7]. This technique allows experimental access to medium-range order structures of amorphous materials that were inaccessible before.

We use DigitalMicrograph™ to control a JEOL-4000EX microscope in our experiments. A DigitalMicrograph script has been written to control the whole experiment. Once an area on the sample is chosen, the script prompts inputs of necessary parameters in the beginning of a session. Then it scans the electron beam through reciprocal space in an interval decided by the operator and takes a dark-field image with each momentum transfer value. Then each dark-field image is saved in a designated folder on the computer attached to the microscope. The same process is typically repeated for several different areas to gain good statistics. Normally a few hundred images are taken in a single experiment.

Another script has been composed to analyze these images. This script opens images in a designated folder on the computer. With each image, it removes distortion caused by modulation transfer in the CCD camera, whose modulation transfer function is pre-measured. Then the script does a Wiener filtering and a frequency filtering. Finally it yields a measured value of the fluctuation of intensity. With the momentum transfer value associated with each image, the intensity fluctuation as a function of the momentum transfer value is eventually obtained.

## Results

Our RDF measurement results on these oxides are given in figure 1. As shown in figure 1, all four oxides have similar short-range order structure, i.e., the average bond length and the average bond angle. This again verifies our point that short-range order is not enough to give a complete description of amorphous structures. The difference in the peak height between the as-grown sample and the rest samples may be due to data analyzing procedures and still does not change our conclusion regarding the short-range order.

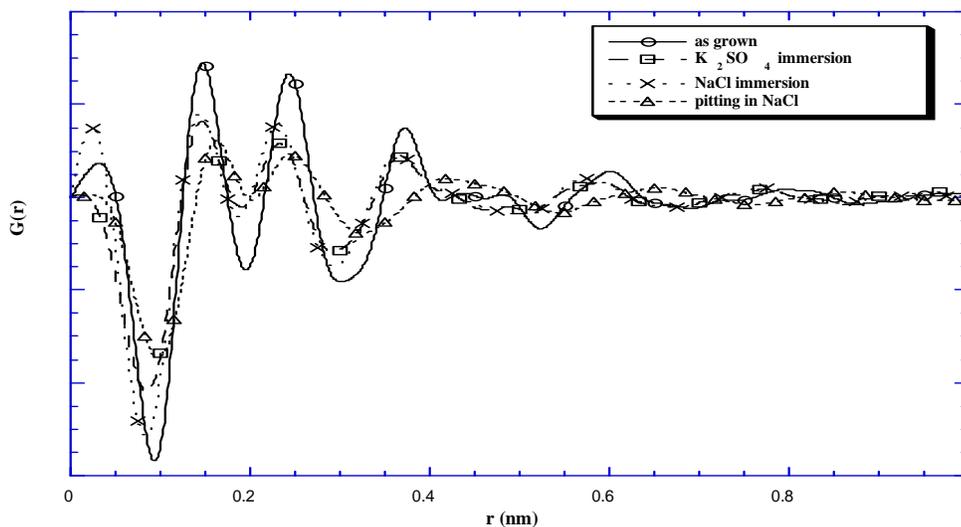


Figure 1. Measured reduced distribution functions show that all four aluminum oxides have similar short-range order structures.

Fluctuation microscopy studies however show significant differences in terms of medium-range order structures in the above samples. The intensity fluctuation these samples is plotted as a function of  $k$  in figure 2. This variance function of  $k$  is directly related to a pair-pair correlation function that defines medium-range order at nanometer scale.

The variance of the as-grown sample has a pronounced peak at about  $5.1 \text{ nm}^{-1}$ . There is actually another peak at about  $8.6 \text{ nm}^{-1}$  which is not shown here due to the cut-off  $k$ -range for this particular as-grown oxide. Such a peak was detected in our data of another normal aluminum oxide sample. As to the immersed samples, the variance has an additional peak at about  $3.2 \text{ nm}^{-1}$ . Interestingly, the film immersed in  $\text{K}_2\text{SO}_4$  solution and that immersed in  $\text{NaCl}$  solution have almost identical medium-range order structures. The sample that went through

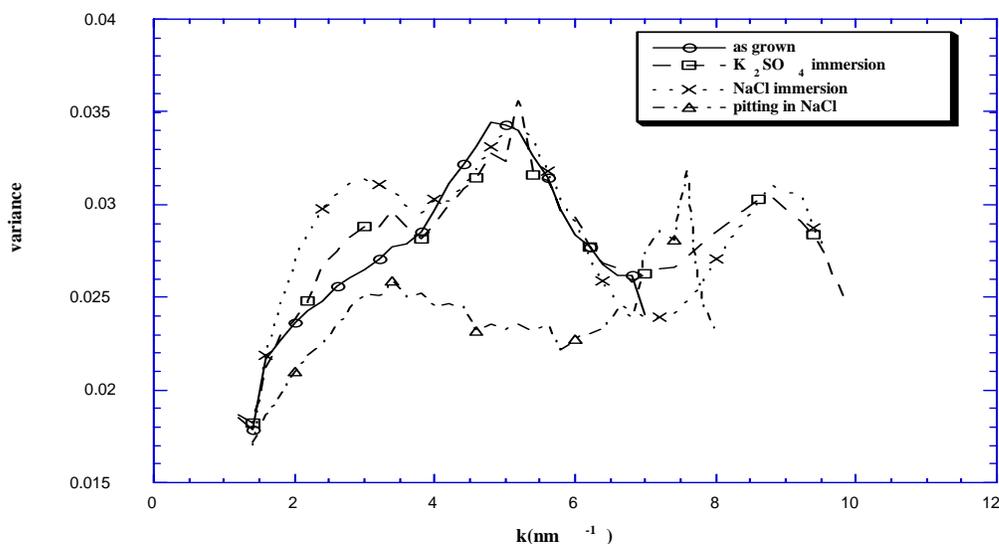


Figure 2. Plots of the variance as a function of  $k$  for four aluminum oxides, sample A, B, C, D. Differences in medium-range order structures are significant.

pitting in  $\text{NaCl}$  solution however has a structure different from those of the rest. Peaks seen in sample A, B, and C are suppressed in the variance function for sample D. Instead, there is a pronounced peak at about  $7.1 \text{ nm}^{-1}$ .

## Discussions

The peak in the as-grown sample (sample A) is positioned at a momentum transfer value close to the (200) reflection of the  $\gamma$  crystalline phase. This confirms a long speculation that the normal amorphous aluminum oxide has a  $\gamma$ -like structure, i.e. there are structure subunits or clusters in the network that are similar to the crystalline unit cells of the  $\gamma$ -phase. This should not be a surprise. Amorphous states and crystalline states are often just different minima of the same thermodynamic free energy of a system.

Our results of samples being through immersion in solutions (sample B immersed in NaCl and sample C in  $K_2SO_4$ ) show that immersion in solution does modify the oxide structure, as there is an additional peak at about  $3.2 \text{ nm}^{-1}$  in sample B and C. This peak is identified as one of the boehmite-like phase. So exposure to  $H_2O$  leads to partial hydroxylation of the oxide and results in a boehmite-like structure. To our surprise, the presence of  $Cl^-$  ions did not make a difference in these two immersion samples. Sample B was immersed in  $K_2SO_4$  solution and sample C was immersed in NaCl solution and yet their structures are very similar. Both of them show an additional boehmite-like peak at the same k value.

The structure in sample D, which went through pitting treatment in NaCl solution, is bayerite-like. The process was to apply a potential on an aluminum anode in NaCl solution. Al corrosion was introduced. It is believed that most aluminum oxides will be converted probably to a hydroxide phase under this condition. Our result supports this belief as sample D shows a bayerite-like structure, which is totally different from those of the other samples and is a hydroxide phase. This might have occurred through precipitation from solution.

## Conclusions

We applied fluctuation microscopy technique to study medium-range order in amorphous aluminum oxides under different treatments. For the first time, we are able to confirm that normal amorphous aluminum oxides have a  $\gamma$ -phase like structure. Our results also show that immersion in solution containing water modifies the oxide.  $Cl^-$  ion presence however is not a contributing factor to this modification. We also observed the conversion of the oxide into a hydroxide phase during aluminum corrosion. In this study, fluctuation microscopy has proven to be a powerful technique to unravel mysteries in amorphous structures and we plan to further our studies by investigating oxides treated under other conditions.

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