Highly charged ion interactions with thin insulating films

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Abstract

The electrical conductance of magnetic tunnel junction (MTJ) devices whose ultra-thin aluminum oxide tunnel barriers were irradiated by highly charged ions (HCIs) increases linearly with the fluence of HCIs, while retaining a current–voltage relationship indicative of a tunnel junction. The slope of the MTJ conductance as a function of fluence varies with different tunnel barrier thicknesses d, levels of oxidation (stoichiometry) and charge state q. Since the MTJ conductance after HCI irradiation is due to tunneling, the increased conductance can result from thinning the barrier, reducing the effective tunnel barrier height φ, or both. Measurements of the current–voltage profile provide sufficient degrees of freedom to explicitly identify two important parameters that dominate the timescales of the interaction: (1) the HCI velocity, which (along with charge state) determines the extent of above-the-surface dynamics, and (2) the target’s effective charge mobility, which controls the relaxation rate for the energy deposited by the HCI. Since the experimental methods utilized (either in real time or post facto), implicitly rely upon forcing as much of the interaction as possible to be at or above the surface, optimization of these surface methods has relied upon minimizing incident velocity and electronic mobility. Therefore, the materials extensively studied are mostly fluorides and oxides (graphite being a notable exception), which have essentially no mobility and are stable enough to facilitate post facto and ex situ examination of surface nanofeatures. These HCI created features, when studied with scanning probes, have typically been found to be either well formed “hillock” structures [3,4] of unknown composition, or caldera like structures [5–7] reminiscent of features created by swift, heavy ions [8] (SHI).

In an effort to access more and different information from the nanofeatures left by HCIs neutralizing on surfaces (or those from SHIs), we have developed a method of fabricating ultra-thin (≈1 nm) aluminum oxide films on a metal surface, irradiating them with HCIs to form nanofeatures, and then depositing another metal on top to form a magnetic tunnel junction (MTJ) device [9,10]. This approach has several notable advantages: (1) allows direct, electrical measurements of the HCI created nanofeatures, (2) encapsulates the nanofeatures to minimize effects due to chemical reaction with the environment or coarsening, thereby creating an archaeological record that can be re-measured many times with different techniques, (3) provides ensemble averages of a large, selectable number of features for each measurement, and (4) integrates over all modifications throughout the thickness of the tunnel barrier, i.e., the measurable interaction volume is not limited to the surface. For all the MTJs fabricated thus far, the electrical conductance of the irradiated MTJs is always seen to increase linearly with fluence, where the slope depends on the material properties of the aluminum oxide and the charge state of the HCI, e.g., see [11–13].

Introduction

Electronic excitations in solids, and even the interaction of swiftly moving charged particles, have been studied for the better part of a century, yet a robust description of the excitation and relaxation processes that occur when a highly charged ion (HCI) neutralizes on a solid surface remains the subject of scientific scrutiny. This is due in part to the unusually large energy densities, e.g., >20 keV/nm³, that are created by the HCI neutralization energy, e.g., see[11–13]. This is due in part to the unusually large energy densities, e.g., see[11–13].

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In this paper, we present electrical measurements collected from HCl irradiated MTJs dosed using Xe\textsuperscript{32+} and Xe\textsuperscript{41+} that illustrate the basic behavior of this method, i.e., the linear increase in conductance with different slopes. The discussion is then focused on the samples irradiated with Xe\textsuperscript{32+} that have a relatively shallow slope corresponding to gentle modification of the tunnel barrier compared to higher charge states. Therefore, the thin barrier limit is avoided and the change in the electrical properties can be reasonably analyzed within a WKB (Wentzel–Kramers–Brillouin) tunneling formalism [14–16]. Using WKB, we extract the effective tunnel barrier parameters as a function of the HCl fluence, which show a systematic decrease in the tunnel barrier thickness while the tunnel barrier height remains essentially constant.

**Experimental**

The MTJ devices are fabricated and irradiated within a system of ultra-high vacuum (UHV) chambers connected with the National Institute of Standards and Technology (NIST) Electron Beam Ion Trap (EBIT), described in more detail elsewhere [17,18]. Thermally oxidized silicon substrates (approximately 1 × 2 cm) are loaded into vacuum and cleaned with an oxygen plasma. A lower electrode structure is deposited through a shadow mask that defines a longitudinal wire and portions of four lateral wires that identify four device locations per substrate. After the lower electrodes, a uniform (unmasked) ultra-thin layer of aluminum is deposited that provides a barrier both on top and on the sides of the lower electrodes. The aluminum is then exposed to an oxygen plasma for a predetermined time known to create a high quality tunnel junction. For each irradiation experiment, several (typically eight) substrates are prepared the day before and stored under UHV conditions overnight allowing the glassy aluminum oxide to sufficiently relax. Three of the four devices per substrate are then sequentially exposed to different fluences of HCIs, followed by immediate (typically <10 min) deposition of the encapsulating upper electrode structure that completes the electrical device. For the samples discussed here, the completed device structure is 2 C\textsubscript{5}O\textsubscript{4}/Al\textsubscript{1}/1.1 A\textsubscript{2}H\textsubscript{2}O\textsubscript{1}[HCl\textsubscript{1}]/10 C\textsubscript{4}/40 C\textsubscript{3}/3 Au; thicknesses are in nm from bottom to top, “+Ox” indicates plasma oxidation, and “[+HCIs]” indicates different fluences of HCl irradiation for each device. The oxygen incorporation into the aluminum layer causes it to expand ∼45% so that the oxidized aluminum is estimated to be ∼1.5(1) nm [19].

Once completed, the substrates are removed from vacuum and measured in a four point configuration by applying constant current and measuring the voltage drop across the MTJ. For current–voltage (I–V) relationship, the current I is sequentially stepped and the voltage V measured at each point. For single point resistance measurements, the electrical resistance $R = V/I$ (conductance $g = 1/V$) and for the I–V measurements $R = dV/dI$ ($g = dI/dV$). In both cases, the resistance (conductance) must be corrected for a geometric “negative resistance” artifact [20]. The cumulative uncertainties in conductance represent a 1 sigma propagation of uncertainties arising from uncertainties in the fluence, device size, negative resistance correction, and zero bias voltage offsets.

**Results**

MTJ electrical conductance $g$ as a function of HCl fluence is shown in Fig. 1 for devices irradiated with Xe\textsuperscript{32+} and Xe\textsuperscript{41+}. Each datum represents a different MTJ device prepared according to the same process recipe but irradiated with a different fluence $N$. The data are then fit with a line to extract the slope of conductance $\sigma_g$, which corresponds to the average conductance of each HCl nanofeature. For the two charge states shown here, $\sigma_g$ is a factor of 200 different even though the HCl potential (neutralization) energies (PE) differ by only a factor of 2 (19.3 keV for Xe\textsuperscript{32+} and 41.7 keV for Xe\textsuperscript{41+}), the velocities by ≈15% and the estimated total (integrated through the ∼1.5 nm tunnel barrier) stopping power by <1% (6.82 keV for Xe\textsuperscript{32+} and 6.89 keV for Xe\textsuperscript{41+}). By way of comparison, a 10 nm\textsuperscript{2} area of the unirradiated MTJ has a conductance of $5 \times 10^{-11}$ S and each nanofeature produced from Xe\textsuperscript{44+} using this device recipe has a $\sigma_g \approx 5 \times 10^{-8}$ S. No evidence has been seen to suggest that the HCl affects the electrical performance of any portion of the device other than the tunnel barrier before coming to rest deep in the device substrate.

These measurements make clear that the nanostructures produced by HCIs have a large electrical conductance. In order to assess whether the HCIs produce holes that penetrate through the barrier, particularly for the MTJ and charge combinations that result in $\sigma_g$ values approaching a conductance quanta, we have performed measurements of the resistance vs. temperature (not shown, see [10]). For metallic through-holes, the resistance should increase with temperature. However, in all devices measured to date, the electrical resistance has always decreased with increasing temperature, characteristic of a tunnel junction. The HCl irradiated devices exhibit a resistance change that is very similar to (but slightly less than) the unirradiated control MTJs and both have a slope that implies the charge transport is occurring through tunneling [21].

To provide additional insight into the characteristics of the transport, the current vs. voltage relationship is measured and the first derivatives are calculated as is shown in Fig. 2. This example is taken from one of the most heavily dosed MTJs using Xe\textsuperscript{32+} and corresponds with device “13A” in Fig. 1. It exhibits a parabolic dependence typically seen in high quality tunnel junctions. (One should note that Joule heating would produce a curvature in the opposite direction.) Therefore, we conclude that in most of the cases (excepting some ultra-thin barriers irradiated with Xe\textsuperscript{44+}) the transport through the HCl produced nano-features is due to tunneling through a potential barrier.

**Discussion**

The data in Fig. 2 can be fit using an expression for the tunnel current density $J$ based on the WKB approximation assuming the...
energy diagram shown as an inset in Fig. 2. This approximation gives \( J \) as a function of voltage [14-16]:

\[
J = \frac{3e}{4\pi\hbar d} \left( \phi_{12}(V) \exp \left[ -Ad\left(\sqrt{\phi_{12}(V)} - (\phi_{12}(V) + eV) \right) \right] 
- \exp \left[ -Ad\left(\phi_{12}(V) + eV\right) \right] \right)
\]

where \( e \) is the electron charge, \( h \) is Planck's constant, \( A = \frac{4\pi\sqrt{2m\phi_{12}}}{\phi_{12}} \approx 1.025 \text{ Å}^{-1} \text{ eV}^{-1/2} \), \( m \) is the electron mass, \( d \) is the tunnel barrier thickness, and \( \phi_{1} \) and \( \phi_{2} \) are the forward and reverse potential barrier heights. By allowing an unequal forward and reverse barrier height \( \phi_{1} \) and \( \phi_{2} \), the model accounts for the asymmetry in the data and the effective barrier height for both forward and reverse bias can be extracted from the fit. As can be seen in the data, the parabolic shape is centered about a voltage that is greater than 0 and is not the same on either side of the center. Both of these are indicators that the tunnel barrier is asymmetric despite the composition of the intended device being...Co/Al+Ox/Co...This asymmetry is also observed in the unirradiated devices, as can be seen in Fig. 3, and is interpreted as a perturbation to the Fermi energy in the underlying Co due to excess oxygen from the aluminum oxidation process.

As is shown in Fig. 2, the data is well fit using Eq. (1) and allows the effective tunneling parameters to be extracted. In previous work [9], we found that the WKB formalism could not be reasonably applied to tunneling measurements when the HCI nano-features severely modified the tunnel barrier, as was the case for Xe32+ irradiation. Further, the low device resistances compared to the much larger electrode resistances in those samples provided substantial technical challenge to applying a sufficient bias (100 mV) across the junction that would allow the cubic part of the current–voltage relationship to be adequately measured. To avoid effects that may arise due to variations in the density of states near the Fermi energy, we always collect data between ±100 mV. Since the Xe32+ data presented in Fig. 1 have a relatively small \( \sigma \), the HCI conductance through these nano-features are still within the range where the WKB formalism may be reasonably applied.

All the Xe32+ irradiated samples and the corresponding control devices shown in Fig. 1 have been fit in the same manner as the example shown in Fig. 2 to extract composite values of the tunnel barrier thickness and the forward and reverse bias barrier heights. These parameter values are shown in Fig. 3 as a function of the number of HCIs. The effective tunnel barrier thickness decreases by more than an Ångstrom over the range of the data. A linear fit establishes the rate of thinning and standard error, as shown, and indicates the observed change is statistically significant. Similarly, the forward bias barrier height \( \phi_{1} \) does not exhibit any change while the reverse bias barrier height \( \phi_{2} \) shows a small upward trend, as determined by comparison with the standard error.

In order to interpret these trends, we will use device “13A” (indicated in Figs. 3a and b) as an example. As is seen in Fig. 1, the zero bias conductance of 13A is 0.13 S after being irradiated with \(~1.19 \times 10^{7}\) Xe32+ ions compared to the unirradiated on-chip control “13D” which had a zero bias conductance of 0.083 S. The...
addition of HCl produced nanostructures with thinner barriers adds more current flow, so that the native barrier and HCl features can be considered as two independent channels. So when the current–voltage relationship is measured in Fig. 2, 41% of the current (0.053 S/0.13 S) is transmitted through the 9160 μm² of unirradiated tunnel barrier and the remaining 59% is transmitted through the dilute density of HCl nanostructures. The fit parameters shown in Fig. 3 are therefore a convolution of the unirradiated tunnel junction and HCl produced tunnel junctions, which we will assume are identical. In attempt to deconvolve these two contributions, we follow Brinkman et al. [14] by expanding Eq. (1) to third order and normalizing the conductance by the zero bias conductance so that:

\[
G_{\text{norm}}(V, \phi_1, \phi_2) = \frac{G(V)}{G(0)}
\]

\[
= 1 - \left( \frac{Ad\phi}{96\pi^2} \right) eV + \left( \frac{A^2 d^2}{4608\pi^2} \right) (eV)^2
\]

where \(\phi = (d_2 - d_1)\) and \(d = \phi_2 - \phi_1\). Taking the measurement as a sum of the two conductance contributions in parallel:

\[
G_{\text{norm}}^{13A}(V) = G_{\text{norm}}^{13D}(V) d_{13D}^{13D} \phi_1^{13D} \phi_2^{13D} + G_{\text{norm}}^{HCl}(V) d_{HCl}^{13D} \phi_1^{HCl} \phi_2^{HCl}
\]

where \(G_{\text{norm}}^{13A}(V)\) is the measurement of 13A, the C values are current weights 0.41 and 0.59, respectively (from above), \(G_{\text{norm}}^{13D}(V, \ldots)\) is the independent measurement of the control 13D that separately yields \(d_{13D}^{13D} \phi_1^{13D} \phi_2^{13D}\) (shown in Fig. 3) leaving \(d_{HCl}^{13D} \phi_1^{HCl} \phi_2^{HCl}\) as unknowns. Since the normalization reduces the number of degrees of freedom to two, we eliminate, \(\phi_1^{HCl}\) by setting it to \(\phi_1^{13D}\) since Fig. 3b indicates that \(\phi_1\) is unchanged by the HCl irradiation. Solving for the two remaining parameters, we find \(d_{HCl}^{13D} = 13.9 \text{ Å}\) and \(\phi_2^{HCl} = 0.84 \text{ eV}\), compared with the convoluted fit values (in Fig. 3) of \(d = 14.7 \text{ Å}\) and \(\phi_2 = 0.83 \text{ eV}\). One might interpret the difference between \(d_{HCl}^{13D} = 13.9 \text{ Å}\) and \(d_{13D}^{13D} = 15.44 \text{ Å}\) as the effective vertical size of the nano-feature, although no direct spatial information is available to support that conclusion. So, in the regime where both current paths (unirradiated barrier and HCl features) contribute non-negligible current, the initial barrier parameters are convolved with the HCl modified ones in a non-obvious way that provides an intermediate parameter value representative of neither. However, the deconvolution scheme used here as an illustration contains both differences and quotations of the data, amplifying the effects of measurement uncertainties, or thicker barriers (where WKB can be done). The integration of an MTJ structure with an HCl irradiated barrier provides a method of probing HCl induced nanostructures with electrical transport techniques. These measurements show that the nano-features are highly conducting compared to the properties of the previously insulating material, but still retain a quantum tunneling current–voltage characteristic. If the tunnel barrier is not too severely modified, as is the case for XeHCl, the WKB approximataion for the tunneling can be applied, revealing a systematic decrease in the effective tunnel barrier thickness while the potential barrier shape trends toward symmetric. To deconvolve the contributions from the unirradiated and irradiated portions of the sample, a simple two current model is implemented that suggests more likely values of the tunnel barrier thickness and effective barrier height for the HCl irradiated portion of the device. While the ability to use the WKB method is limited by small perturbations to the tunnel barrier, the ability to separate the two source of currents depends on high signal-to-noise, which is contradictory to using samples with weak perturbations. Application of this approach to data sets with greater dynamic range, smaller measurement uncertainties, or thicker barriers (where WKB can be used for larger perturbations) may offer a low uncertainty determination of the tunnel parameters.

References