Tunable Nanometer Electrode Gaps by MeV Ion Irradiation

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We report the use of MeV ion-irradiation-induced plastic deformation of amorphous materials to fabricate electrodes with nanometer-sized gaps. Plastic deformation of the amorphous metal Pd80Si20 is induced by 4.64 MeV O2+ ion irradiation, allowing the complete closing of a sub-micrometer gap. We measure the evolving gap size *in situ* by monitoring the field emission current-voltage (I-V) characteristics between electrodes. The I-V behavior is consistent with Fowler-Nordheim tunneling. We show that using feedback control on this signal permits gap size fabrication with atomic-scale precision. We expect this approach to nanogap fabrication will enable the practical realization of single molecule controlled devices and sensors.
In nanostructure fabrication, it is often a challenge to precisely control and characterize critical dimensions, such as the size of a gap between two metallic electrodes. Such a structure is fundamental for nanoscale electronic devices, including those with small molecules in the gap that may become essential components of future devices, and long molecules such as DNA that may lend themselves to extremely rapid sequencing through their electrical signals\(^1\). A variety of methods has been used for the fabrication of electrodes with a nanometer-sized gap: mechanical break junctions\(^2\), electron-beam deposition\(^3\), oblique evaporation through a lift-off mask\(^4\), electrochemical deposition\(^5,6\), electromigration\(^7\), electron-beam lithography\(^8,9\), and focused-ion-beam lithography\(^10\). With some of these methods, the gap has been controlled by measuring the electrical properties of electrodes \textit{in situ}\(^2,4-6\).

Amorphous materials, such as SiO\(_2\) or Pd\(_{80}\)Si\(_{20}\), are known to be deformed plastically by MeV ion irradiation\(^11-14\). The electronic energy loss of the incoming MeV ions causes an anisotropic deformation consisting of an increase in the sample dimensions perpendicular to the ion beam and a decrease in the dimension parallel to the ion beam\(^15\). Induced strains accumulate with increasing ion beam fluence and can exceed unity, causing microns of dimensional changes. Hence, the phenomenon can be used for precise nanostructure fabrication if \textit{in situ} feedback control can be implemented based on some physical quantity such as a tunneling current reflecting a critical dimension.

In this Letter, we demonstrate that we can fabricate amorphous metallic Pd\(_{80}\)Si\(_{20}\) electrodes with a nanometer-sized gap by using MeV oxygen ion irradiation-induced plastic
deformation. We also demonstrate that the gap size can be controlled with nanometer precision by *in situ* feedback control using the field-emission current between the electrodes.

We prepared a layered Pd$_{80}$Si$_{20}$/SiO$_2$/Si structure with an H-shaped trench, as shown in Fig. 1. A 500 nm thick SiO$_2$ layer was grown by thermal oxidation of a Si substrate and then a 200 nm-thick Pd$_{80}$Si$_{20}$ film was deposited by Ar$^+$ ion beam sputtering from a target of the same composition. The H-shaped trench was micromachined using a 50 keV Ga$^+$ beam from a Micron 9500 Focused Ion Beam instrument. The trench width was ~800 nm. The milled depth was ~1.1 μm, so that the lower part of the side walls visible in Fig. 1(a) corresponds to the silicon substrate. Irradiation at normal incidence with 4.64 MeV O$^{2+}$ ions was performed either at room temperature (RT) or at liquid nitrogen temperature (~80 K) with the use of a General Ionex 1.7 MV tandem accelerator. The beam spot was 1 mm in diameter and the beam current was typically ~6 nA. The pressure in the irradiation chamber was roughly 10$^{-5}$ Pa. The energy of the incident oxygen ions was high enough to allow the ions to penetrate through the Pd$_{80}$Si$_{20}$/SiO$_2$ bilayer and come to rest within the Si substrate$^{16}$. Every sample was characterized before and after irradiation by using scanning electron microscopy (SEM). Moreover, the cross section of some samples was studied with atomic force microscopy (AFM).

Figure 1(b) shows an SEM image of the sample irradiated with $1\times10^{16}$ ions/cm$^2$ at RT. Plastic deformation due to the ion irradiation was observed in both Pd$_{80}$Si$_{20}$ and SiO$_2$ layers. The walls surrounding the gap deform into the gap in all directions. The SiO$_2$ walls become especially quite rounded and are almost in contact, indicating that the SiO$_2$ deformation rate is larger than that of Pd$_{80}$Si$_{20}$ under these conditions. We observed no dimensional modification to
the crystalline silicon substrate from this treatment. From SEM images, we evaluated and compared the relative width change of the gap of Pd$_{80}$Si$_{20}$ and SiO$_2$ in the bilayered structure as a function of the irradiation fluence. Figure 2 shows a comparison of the width changes for irradiations at RT and 80 K. At RT and 80 K, SiO$_2$ deforms almost three times and about two times as much, respectively, as does Pd$_{80}$Si$_{20}$. In all cases, the gap width decreases almost linearly with ion fluence. Moreover, low temperature irradiation induces more significant deformations of Pd$_{80}$Si$_{20}$ and SiO$_2$ compared with those obtained at RT. We have previously demonstrated that this kind of deformation does not occur in the case of a crystalline pure metal (Al, Au) on top of a similar SiO$_2$ layer$^{17}$.

From Fig. 2 it is apparent that, at least for RT irradiations, the Pd$_{80}$Si$_{20}$ gap width saturates once the SiO$_2$ gap is closed. This result indicates that the Pd$_{80}$Si$_{20}$ gap closure is restrained by the complete closure of the underlying SiO$_2$ gap (see Fig. 1(b)). To eliminate this restraint, we dipped the irradiated sample in a H$_2$O:HF = 10:1 solution, which removed the SiO$_2$ underneath the Pd$_{80}$Si$_{20}$ gap. In Fig. 1(c) is the SEM image of the same sample from Fig. 1(b) after it has been etched in diluted HF for 4 minutes. The SiO$_2$ gap is open again up to the same width as the silicon gap (800 nm), and the etched SiO$_2$ gap is wider than that of the Pd$_{80}$Si$_{20}$ (~500 nm), which is not affected by the etching. Next, we chose a second irradiation treatment under conditions expected to completely close the gap based on the data in Fig. 2: $1\times10^{16}$ ions/cm$^2$ at 80 K. Figure 1(d) shows an SEM image of the resulting sample. Not only has the Pd$_{80}$Si$_{20}$ gap been completely closed, but also the deformation of the free-standing portion of the Pd$_{80}$Si$_{20}$ layers has been large enough to cause buckling.
For controlling the gap separation with nanometer precision, we prepared another type of sample: a layered structure of Si$_3$N$_4$/SiO$_2$/Si with Pd$_{80}$Si$_{20}$ electrodes, as illustrated in Fig. 3(a). A 200 nm thick Si$_3$N$_4$ film was grown by chemical vapor deposition on a 500 nm thick SiO$_2$ layer grown by thermal oxidation of a Si wafer. A Pd$_{80}$Si$_{20}$ line, 100 nm thick and 3 μm wide, was prepared by Ar$^+$ ion beam sputtering, photolithography and lift-off techniques. Then the line was cut using the FIB. In order to minimize the influence of the underlying SiO$_2$ layer on the deformation of the Pd$_{80}$Si$_{20}$ electrodes, the SiO$_2$ layer was etched in a buffered HF solution for 3.5 minutes and then in a H$_2$O:HF = 50:1 solution for 5 minutes. Figure 3(b) shows an SEM image of the electrodes displaying a gap of about 130 nm.

We monitored the I-V characteristics of the pair of electrodes during O$^{2+}$ irradiation at RT. The ion irradiation was paused between incremental ion doses while I-V behavior was characterized over a series of ion irradiation fluences. The results for the series are shown in Fig. 4. Each curve shows the characteristics of field emission, and the abrupt current rise shifts to lower voltage with increasing ion irradiation fluence. These results indicate that the change in the I-V characteristics with fluence reflects a continuous shrinkage of the electrode separation with increasing fluence. This interpretation is confirmed by Fig. 3(c), taken after the final irradiation fluence in Fig. 4 and showing that the gap between the Pd$_{80}$Si$_{20}$ electrodes is almost completely closed after an irradiation with $5.65 \times 10^{15}$ ions/cm$^2$ at RT. Although Fig. 3(c) indicates that the Si$_3$N$_4$ layer has been deformed in addition to the Pd$_{80}$Si$_{20}$ layer, detailed SEM observations not reproduced here confirmed that the gap between the Si$_3$N$_4$ layers was still open after this fluence.
According to elementary Fowler-Nordheim theory\textsuperscript{18,19}, the relation between the emission current $I$ and the applied voltage $V$ can be written in the following logarithmic form:

\[
\ln \frac{I}{V^2} = \ln \left[ \frac{e^3}{16\pi^2 \hbar \phi L^2} \right] - \frac{4\sqrt{2m}}{3e\hbar} \phi^{3/2} \frac{L}{V},
\]

(1)

where $e$ is the elementary positive charge, $m$ is the electron mass, $\hbar$ is the Planck’s constant divided by $2\pi$, $\phi$ is the work function, $S$ is the emission area and $L$ is the gap. In this equation, the exchange-and-correlation interaction between the emitted electron and the surface is neglected and a simple triangular barrier (i.e., spatially uniform field near the emitter tip) is assumed. According to Equation 1, for field emission, a "F-N plot" of $\ln(I/V^2)$ vs. $1/V$ should exhibit linear behavior. The F-N plots of our data (not reproduced here) yielded nearly straight lines. A linear least-squares fit of $\ln(I/V^2)$ vs. $1/V$ yielded parameters used to construct the (nonlinear) dashed curves superposed on the data in Fig. 4. The good agreement illustrated in Fig. 4 indicates that the observed $I-V$ characteristics can be attributed to field emission. Although the three variables $(S, L, \phi)$ appear in Equation (1) in only two combinations, $(S/(\phi L^2))$ and $(L\phi^{3/2})$, we identify unique values of all three variables as described below. The coefficient of $1/V$ in Equation (1) depends on both $L$ and $\phi$; however, we presume that the fluence dependence of the coefficient of $1/V$, i.e., the slope of the line in the F-N plot, reflects a change only in the gap distance because we presume the work function of Pd$_{80}$Si$_{20}$ is not changed by MeV ion irradiation (after, perhaps, an initial transient). When plotted as a function of the fluence, the coefficient of $1/V$ in Equation (1) increases linearly with irradiation fluence and is almost zero at $5.65 \times 10^{15}$ ions/cm$^2$ (not shown). This is consistent with the result shown in Fig. 2 that the gap width decreases almost
linearly with ion fluence, and supports our presumption. Thus, if we once determine by any means a value of $\phi$ at any particular value of $L$, we can uniquely determine the three variables ($S$, $L$, $\phi$) at any irradiation fluence. We did not obtain any experimental value of $L$ during the experiment reported in Fig. 4. However, in a similar experiment with a known gap distance of 10 nm, the I-V characteristic fit Equation (1) with $\phi = 5.7$ eV. Assuming $\phi$ does not vary from sample to sample permits us to apply this value to the data in Fig. 4 and thereby uniquely determine all three parameters.

The quantitative analysis of tunneling I-V curves permits exquisite measurement and control of gap dimensions. The typical increment of irradiation fluence in the present experiment is $6 \times 10^{13}$ ions/cm$^2$, which corresponds to a 1.2 nm decrease in gap distance. The scatter in the data and the quality of the fit are sufficiently good that cutting the fluence increment by a factor of six, to $1 \times 10^{13}$ ions/cm$^2$, corresponding to gap changes of 0.2 nm, should result in distinguishable $I$-$V$ curves - especially for the smallest gaps. Hence we believe that these results demonstrate fabrication precision at the scale of the diameter of an individual atom.
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Author Contributions

All of the authors designed the experiments and analyzed the data. J.C. Ch.-W., K.N., and G.M.S. performed the experiments. All authors discussed the results.

References


Figure Legends

FIG. 1. SEM images of an H-shaped structure milled in a bilayered Pd$_{80}$Si$_{20}$ (200 nm)/SiO$_2$ (500 nm)/Si sample: (a) before irradiation. (b) after irradiation with $1\times10^{16}$ ions/cm$^2$ at RT. (c) same as in (b) but after etching in HF for 4 minutes. (d) after etching and an additional irradiation with $1\times10^{16}$ ions/cm$^2$ at ~80 K. The original FIB milled depth and gap size are ~1.1 μm and ~800 nm, respectively. The sketch at the top is a schematic cross section of the sample.

FIG. 2. Comparison of width change of each gap of SiO$_2$ and Pd$_{80}$Si$_{20}$ in the bilayered structure as a function of ion fluence for irradiations at RT and at 80 K. The line is a guide for the eyes.

FIG. 3. (a) Schematic diagram of the two electrodes. SEM images of the electrodes: (b) before irradiation and (c) after irradiation with $5.65\times10^{15}$ ions/cm$^2$ at RT.

FIG. 4. Fluence dependence of the I-V characteristics at RT. The I-V curve measured after irradiation with $5.65\times10^{15}$ ions/cm$^2$ is shown in a different horizontal scale. Dashed lines are obtained by a least-squares fit to Equation (1). The best-fit gap distance corresponding to each I-V curve is as follows: ♦: 0.006 nm, ◇: 1.8 nm, ▽: 3.0 nm, ▼: 4.2 nm, ■: 5.4 nm, □: 6.5 nm, ▲: 8.3 nm, △: 8.5 nm.