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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.

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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 signals¹. A variety of methods has been used for the fabrication of electrodes with a nanometer-sized gap: mechanical break junctions², electron-beam deposition³, oblique evaporation through a lift-off mask⁴, electrochemical deposition^{5,6}, electromigration⁷, electron-beam lithography^{8,9}, and focused-ion-beam lithography¹⁰. With some of these methods, the gap has been controlled by measuring the electrical properties of electrodes *in situ*^{2, 4-6}.

Amorphous materials, such as SiO₂ or Pd₈₀Si₂₀, are known to be deformed plastically by MeV ion irradiation¹¹⁻¹⁴. 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 beam¹⁵. 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 *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 Pd₈₀Si₂₀ 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 Pd₈₀Si₂₀/SiO₂/Si structure with an H-shaped trench, as shown in Fig. 1. A 500 nm thick SiO₂ layer was grown by thermal oxidation of a Si substrate and then a 200 nm-thick Pd₈₀Si₂₀ 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 Micrion 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 O²⁺ 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 Pd₈₀Si₂₀/SiO₂ bilayer and come to rest within the Si substrate¹⁶. 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 1×10¹⁶ ions/cm² at RT. Plastic deformation due to the ion irradiation was observed in both Pd₈₀Si₂₀ and SiO₂ layers. The walls surrounding the gap deform into the gap in all directions. The SiO₂ walls become especially quite rounded and are almost in contact, indicating that the SiO₂ deformation rate is larger than that of Pd₈₀Si₂₀ 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 Pd₈₀Si₂₀ and SiO₂ 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, SiO₂ deforms almost three times and about two times as much, respectively, as does Pd₈₀Si₂₀. In all cases, the gap width decreases almost linearly with ion fluence. Moreover, low temperature irradiation induces more significant deformations of Pd₈₀Si₂₀ and SiO₂ 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 SiO₂ layer¹⁷.

From Fig. 2 it is apparent that, at least for RT irradiations, the Pd₈₀Si₂₀ gap width saturates once the SiO₂ gap is closed. This result indicates that the Pd₈₀Si₂₀ gap closure is restrained by the complete closure of the underlying SiO₂ gap (see Fig. 1(b)). To eliminate this restraint, we dipped the irradiated sample in a H₂O:HF = 10:1 solution, which removed the SiO₂ underneath the Pd₈₀Si₂₀ 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 SiO₂ gap is open again up to the same width as the silicon gap (800 nm), and the etched SiO₂ gap is wider than that of the Pd₈₀Si₂₀ (~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: 1×10^{16} ions/cm² at 80 K. Figure 1(d) shows an SEM image of the resulting sample. Not only has the Pd₈₀Si₂₀ gap been completely closed, but also the deformation of the free-standing portion of the Pd₈₀Si₂₀ 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 $\text{Si}_3\text{N}_4/\text{SiO}_2/\text{Si}$ with $\text{Pd}_{80}\text{Si}_{20}$ electrodes, as illustrated in Fig. 3(a). A 200 nm thick Si_3N_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 $\text{Pd}_{80}\text{Si}_{20}$ 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 $\text{Pd}_{80}\text{Si}_{20}$ electrodes, the SiO_2 layer was etched in a buffered HF solution for 3.5 minutes and then in a $\text{H}_2\text{O}:\text{HF} = 50:1$ 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 $\text{Pd}_{80}\text{Si}_{20}$ electrodes is almost completely closed after an irradiation with 5.65×10^{15} ions/ cm^2 at RT. Although Fig. 3(c) indicates that the Si_3N_4 layer has been deformed in addition to the $\text{Pd}_{80}\text{Si}_{20}$ layer, detailed SEM observations not reproduced here confirmed that the gap between the Si_3N_4 layers was still open after this fluence.

According to elementary Fowler-Nordheim theory^{18,19}, the relation between the emission current I and the applied voltage V can be written in the following logarithmic form:

$$\ln \frac{I}{V^2} = \ln \left[\frac{e^3}{16\pi^2 \hbar \phi} \frac{S}{L^2} \right] - \frac{4\sqrt{2m}}{3e\hbar} \phi^{3/2} \frac{L}{V}, \quad (1)$$

where e is the elementary positive charge, m is the electron mass, \hbar is the Planck's constant divided by 2π , ϕ 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 , ϕ) 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 ϕ ; 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 $\text{Pd}_{80}\text{Si}_{20}$ 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 5.65×10^{15} ions/cm² (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 ϕ at any particular value of L , we can uniquely determine the three variables (S , L , ϕ) 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 ϕ 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 6×10^{13} ions/cm², 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 1×10^{13} ions/cm², 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.

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Figure Legends

FIG. 1. **SEM images of an H-shaped structure milled in a bilayered Pd₈₀Si₂₀ (200 nm)/SiO₂ (500 nm)/Si sample:** (a) before irradiation. (b) after irradiation with 1×10^{16} ions/cm² at RT. (c) same as in (b) but after etching in HF for 4 minutes. (d) after etching and an additional irradiation with 1×10^{16} ions/cm² at ~ 80 K. The original FIB milled depth and gap size are ~ 1.1 μ m 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 SiO₂ and Pd₈₀Si₂₀ 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 5.65×10^{15} ions/cm² at RT.

FIG. 4. **Fluence dependence of the I-V characteristics at RT.** The I-V curve measured after irradiation with 5.65×10^{15} ions/cm² 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: \blacklozenge : 0.006 nm, \diamond : 1.8 nm, \blacktriangledown : 3.0 nm, ∇ : 4.2 nm, \blacksquare : 5.4 nm, \square : 6.5 nm, \blacktriangle : 8.3 nm, \triangle : 8.5 nm.







