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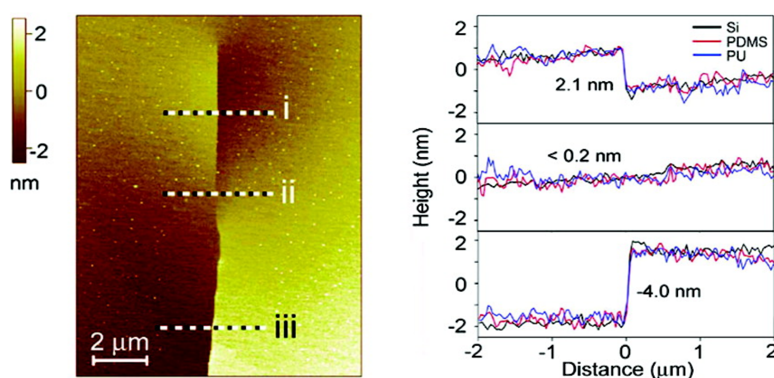

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Approaching Zero: Using Fractured Crystals in Metrology for Replica Molding

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This communication describes a convenient method for the generation of relief features with vertical dimensions ranging from the microscale to the atomic scale using partially fractured, single-crystalline silicon substrates. We used these structures as masters to test the limits of replication of soft lithography and demonstrate the successful replication of features with vertical dimensions down to 0.4 nm.

New techniques for fabricating structures with nanometer dimensions, and especially techniques based on replica molding in polymers, have become important in nanoscience and technology.[1−6] It is, however, difficult (if not impossible) to fabricate masters below 5 nm using the methods most commonly used in nanoscience (e.g., electron beam or focused ion beam lithography). Rogers et al. have, however, demonstrated the replication of features with both lateral and vertical dimensions below 2 nm using single-walled carbon nanotubes (SWNTs) as masters.[7] They optimized conditions for replication and carefully analyzed the limits of replication. SWNTs are, however, impractical as masters for most applications because they have a limited range of sizes (5 nm to <1 nm) and can be difficult to position, manipulate, and locate on a substrate.

This communication demonstrates the generation of features with vertical dimensions down to the atomic scale through fracture of single-crystalline silicon wafers.[8,9] These cracks are characterized by the following attributes: (i) They are continuous steps of smoothly decreasing height, which run in approximately straight lines (<100 μm lateral deviation) along crystal planes. (ii) The edges of the steps at the cracks are typically ∼10 μm in height at the edge of the wafer (where they initiate) and decrease continuously to 0 nm at the "tip" of the crack (where they disappear into the smooth surface of the silicon wafer; hence "approaching zero"). (iii) The fact that these steps are continuous and linear makes them easy to characterize. They are particularly useful since they are easy to *locate*: locating nanoscale features on a macroscale substrate can be a nontrivial and tedious task; these cracks are easily followed from their initiation (a microscale step) to their termini.

Cracks in single-crystalline Si are ideal masters for probing the limits of replication. Their profile—a lateral width that is very small (a number we cannot measure quantatively because of the unknown but broad tip of the AFM) and a vertical step bounded by two flat surfaces—minimizes artifacts in measurement reflecting the interaction of the tip with features that are small laterally. The vertical range in the step height is *uniquely* suited for testing the limits of replica molding because it spans a size range of approximately 10^4 (<1 nm to ∼10 μm); this range would previously only have been accessible through use of multiple masters.

As an example of the use of the step, we examined the use of these step edges as masters for probing the limits of replica molding using "hard" poly(dimethylsiloxane) (h-PDMS) and polyurethane (PU). Commercially available, single-crystalline silicon wafers (two- or three-inch p- and n-doped silicon wafers with ∼2-nm layers of native silicon oxide) were used as substrates. Figure 1A describes

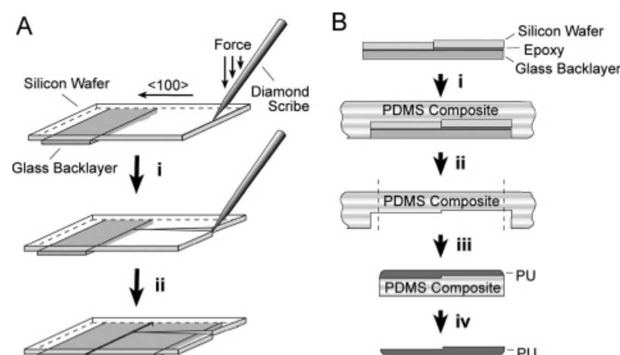

Figure 1. (A) Schematic diagram of the cracking process depicting fracture of a single-crystalline silicon wafer with an epoxy-bonded glass backlayer. The glass backlayer acted both to stabilize the crack and to limit its propagation. (i) We initiated the crack with the tip of a diamond scribe along the ⟨100⟩ direction of the Si wafer. (ii) A second piece of glass, glued to the wafer underneath the crack, provided added stability. (B) Schematic diagram of the process of replication: (i) coating the crack with a PDMS composite and curing, (ii) removing and triming the resultant PDMS stamp, (iii) spin-coating PU onto the PDMS stamp, and (iv) curing and peeling off the PU replica. The dimensions of the Si wafers were typically 1 mm × ∼1 cm × ∼2 cm ($h \times w \times l$). In both diagrams, the dimensions of the crack are exaggerated for clarity.

the preparation and fracture of the silicon wafers. A glass slide (1-mm thick) was bonded with epoxy to the *backside* of a commercially available silicon wafer to stabilize and prevent complete fracture of the wafer by dissipating the mechanical energy of fracture into plastic deformation of the backing polymer and, thus, to terminate the advance of the crack tip. We initiated the crack by applying light pressure by hand at the edges of the wafers with a diamond scribe. The applied pressure was vertical to the plane of the wafer. The crack propagated only to the vicinity of the boundary defined by the glass backlayer; thus, the length of the crack could be controlled to within a few millimeters by the position of the glass slide. After cracking the wafer, we bonded a second glass slide to the backside of the cracked region with epoxy; this slide froze the crack and prevented further growth. Fractured Si, stabilized by binding to a glass backlayer, is remarkably robust: it can, for example, withstand spin speeds in excess of 2000 rpm without noticeable crack propagation.

We transferred the relief structure of the crack, sequentially, to two different polymers using techniques described previously for soft lithography (Figure 1B).[3] The replication process was accomplished in three steps: (1) generation of the crack in silicon, (2) fabrication of a composite, elastomeric stamp using the cracked wafer as a master, and (3) replication of the relief structure of the crack from the composite PDMS stamp using hard, UV-curable PU. The composite stamp comprised an ∼100-μm layer of h-PDMS in direct contact with the surface and a ∼2-mm-thick layer of "soft"-poly(dimethylsiloxane) (s-PDMS) as a backlayer.[4,10,11]

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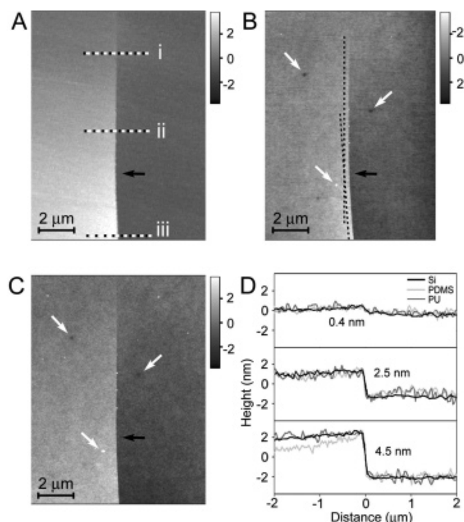

Figure 2. (A) AFM image of a crack in Si. (B) AFM image of a PDMS replica of the same crack. The image has been inverted in contrast and flipped horizontally so that it can be directly compared to the Si master and to the PU replica. The vertical dashed lines are guides for the eye to show the kink in the crack. (C) AFM image of a PU replica produced with the PDMS mold. In A−C, the black arrows indicate the point of inflection that has been used to ensure proper alignment of the AFM scans. The defects of unknown structure labeled with white arrows in B and C can also be used as fiducials. (D) Line scan cross sections of Si, PDMS, and PU at the locations indicated by dashed lines in A−C, showing the smooth decrease in step height with approach to the crack tip.

Figure 2A shows the AFM image of the tip of a crack in silicon. Within 100 μm of the tip, there is no perceptible—within the resolution of our AFM—gap between the two Si planes. This observation suggests that the crack forms by a slip dislocation along a (100) plane, rather than in-plane separation of the silicon along the crack. The dashed lines in the figure indicate locations along the crack at which we measured surface profiles. For this crack, a kink in the crack close to the tip provided a point of reference for comparison between master, mold, and replica.

Figure 2B shows the AFM image of the replicated crack in PDMS. The absence of an upraised spike along the ridge of the crack indicates that there is minimal penetration of the PDMS prepolymer between the faces of the crack. We attribute the bright and dark spots, marked in the image with white arrows, to dust particles or air bubbles, inadvertently acquired during the molding process. Since these types of defects are always present, they also can act as fiducials when there are no obvious markers in the master (e.g., kinks or inversion points). Figure 2C shows the AFM image of a replica in PU, produced using the PDMS stamp. Figure 2D shows individual cross sections for the Si, PDMS, and PU samples, for direct comparison, at each of the three positions marked in Figure 2A. The height of the step remains the same across master, mold, and replica, down to $<$0.4 nm.

Figure 3 shows a plot of step height versus distance along the crack. In these experiments, with our AFM, the step height for Si could be resolved down to $\sim$0.2 nm, the level of roughness of the polished Si substrate (that is, the step became indistinguishable from noise at this level). To account for the inherent roughness of the flat, adjacent regions of the silicon wafer, we took the step height as the difference between corresponding linear fits of the profile data for 1-μm regions on each side of the crack. From these fits, we also determined the average root-mean-squared (rms) roughness

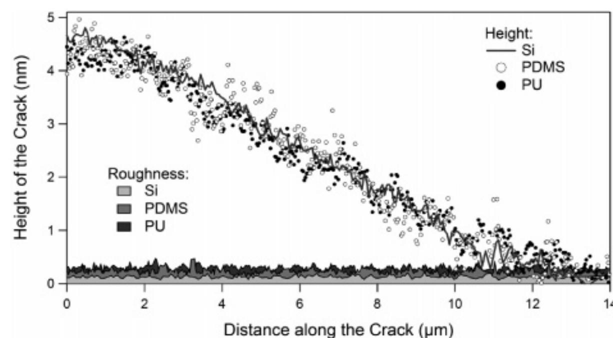

Figure 3. Plot of step height and roughness versus distance along the crack shown in Figure 2. The surfaces extending 1 μm on both sides of the crack were used to generate two linear fits. Step height was taken as the difference between these two linear fits where they crossed a vertical line through the center of the crack. Roughness was determined as the rms deviation from the linear fits.

for these regions (Si = 0.13 ± 0.03 nm, PDMS = 0.23 ± 0.05 nm, PU = 0.30 ± 0.05 nm). There is an initial large increase in roughness (2×) from the crystalline master to the elastomeric mold, but a negligible increase in roughness from PDMS to PU. The height of the replicated crack could be resolved within $\sim$0.4 nm; this limit reflects the roughness of the polymer substrates ($\sim$0.25 nm).

The generation of cracks using this procedure is straightforward and high yielding: close to 100% of the samples generate useful steps. The wide availability of high-quality Si wafers (due to their use in the semiconductor industry) and the ease of generation of the crack and step (which does not require a clean room or specialized equipment) make this approach attractive for wide use in nanoscience. This type of method, accurate, quick, and inexpensive, is attractive because it is highly accessible to the general scientific community. The fact that the nanoscale and subnanoscale features can be located simply by following the crack is also an enormous experimental convenience that is not easily duplicated by nanolithographic or proximal probe techniques.

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Supporting Information Available: Additional AFM data and a detailed description of experimental methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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