Applied Surface Science 362 (2016) 49–55

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

The adhesion behavior of carbon coating studied by re-indentation during in situ TEM nanoindentation

Xue Fan, Dongfeng Diao*

Institute of Nanosurface Science and Engineering (INSE), Shenzhen University, Nanhai Ave. 3688, Shenzhen 518060, Guangdong, China

ARTICLE INFO

Article history:
Received 30 September 2015
Accepted 20 November 2015
Available online 25 November 2015

Keywords:
Adhesion
Re-indentation
Carbon coating
In-situ nanoindentation
Transmission electron microscope

ABSTRACT

We report a nanoscale adhesion induced nano-response in terms of re-indentation during in situ transmission electron microscope (TEM) nanoindentation on the carbon coating with silicon substrate. The adhesive force generated with nanoindentation was measured, and re-indentation phenomenon during unloading with displacement sudden drop and external loading force change from tension to compression was found. The occurrence of re-indentation during unloading was ascribed to the adhesive force of the contact interface between the indenter and the coating surface. Adhesion energies released for re-indentation processes were quantitatively analyzed from the re-indentation load–displacement curves, and carbon coating reduced the impact of adhesion for silicon substrate. The adhesion induced nano-response of contact surfaces would affect the reliability and performance of nano devices.

1. Introduction

Carbon coatings have brought bright prospect in the development of nano devices, since the unique carbon structure of graphene, fullerene, carbon nanotube results in a combination of desirable mechanical [1], tribological [2,3], electrical [4], magnetical [5,6], and optical [7] properties. For its application on novel functional carbon based nano devices, the adhesive force at two contacted solid surfaces plays an essential role to determine the performance of nano devices, for example the tribotronic devices [8] convert the mechanical energy from contact-separation or relative movement into electricity or electrostatic potential [9,10], while adhesion between two material surfaces will prevent relative motion [11]. The adhesive force can be large enough to have influences at nanoscale contact on biological samples [12] and polymer films [13]. Therefore, it is important to study the adhesive properties of the coating surface as well as the adhesion induced nano-response in terms of any sudden movement at nanoscale.

The study of adhesion was often extracted from the pull-off force for tips in contact with flat substrates by means of atomic force microscope (AFM) measurements [14–16] or theoretical molecular dynamics (MD) simulations [17–19]. Such contact does not involve in the elastic-plastic deformations. During nanoindentation contact, the indentation force results from the addition of adhesive and elastic forces at the indenter-sample contact [20,21]. As the critical indentation depth decreases to nanoscale, the effect of adhesion has to be considered [22]. In situ nanoindentation in transmission electron microscope (TEM) enables the real-time observation of deformation and simultaneous measurement of load–displacement behavior [23–27]. By using the in situ nanoindentation, the adhesion at the actual indent region can be measured and directly observed, which provides an effective way to study the adhesion of the two contact surface in nano devices. However, in situ observations of nanoscale adhesion on coating substrate have not been reported yet.

In this paper, we report an in situ TEM observation of adhesion induced re-indentation of carbon coating. The carbon coating was fabricated on silicon wedge substrate by electron cyclotron resonance (ECR) plasma sputtering. Focused ion beam was used to fabricate carbon coated silicon pillar specimens for in situ TEM nanoindentation tests, which were carried out in displacement controlled mode. The loading and unloading processes were in situ observed and the load–displacement curves were recorded. Re-indentation phenomena during unloading for the nano-response of adhesion was investigated and the adhesion energies of different re-indentation loops were quantitatively analyzed.

2. Experiments

2.1. Sample preparation

The carbon coating was prepared on a polished silicon wedge substrate (p-type ⟨1 0 0⟩) by the electron cyclotron resonance (ECR) plasma sputtering method [28]. Magnetic field and microwave

* Corresponding author. Tel.: +86 755 26902415.
E-mail address: dfdiao@szu.edu.cn (D. Diao).

http://dx.doi.org/10.1016/j.apsusc.2015.11.196
0169-4332/

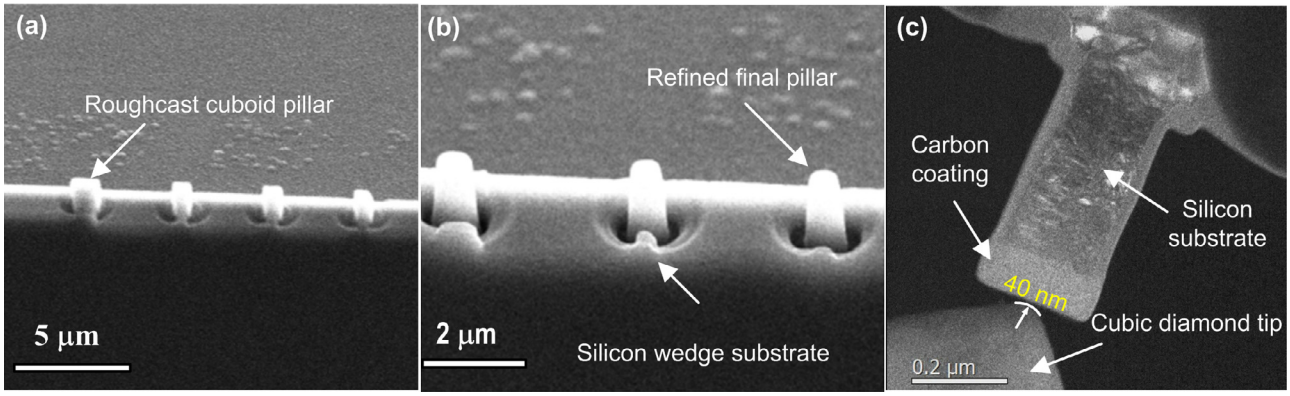

Fig. 1. (a) and (b) The FIB processing to fabricated carbon coated silicon pillar specimens for in situ nanoindentation tests with roughcasts pillar processing and refinement pillar processing, respectively. (c) The dark-field TEM image of the indenter and the carbon coated silicon pillar (coating thickness of 120 nm) before in situ nanoindentation test.

were combined to generate argon plasma. Silicon wedge substrate was pre-sputtered prior to deposition by 3 min etching to remove any residual contaminants. Then, carbon atoms were consequently sputtered off the target and carbon coatings with thickness of 120 nm and 20 nm were prepared by applying a substrate bias voltage. After coating deposition, the ECR carbon coating on silicon samples were micromachined to pillar specimens for in situ nanoindentation tests by using a FEI Helios Nanolab 600 focused ion beam (FIB). First, the sample was FIB milled to rectangle roughcasts pillar with an initial geometry of 500 nm in width, 500 nm in thickness and 800 nm in length, as shown in Fig. 1(a). During this stage, 30 kV ion accelerating voltage and 93 nA FIB current was applied. Then take coating thickness and pillar specimen size into consideration, two pillar specimen of different sizes were processed by refinement operation and fine machining under 15 kV ion accelerating voltage and 43 pA FIB current. Coating with 20 nm thickness had dimensions of 250 nm × 250 nm × 720 nm, and coating with 120 nm thickness had dimensions of 250 nm × 250 nm × 450 nm, respectively, the latter one observed by scanning electron microscope is shown in Fig. 1(b). One thing should be noticed that ultralow FIB current of 43 pA was applied during the finishing stage to avoid possible damages (including ion doping) or thermal recrystallization caused by ion bombardments.

2.2. In-situ nanoindentation

In situ nanoindentation tests were carried out inside a JEOL JEM-2100F TEM using the Hysitron PI95 PicoIndenter. A Boron-through-doped diamond cube corner indenter with curvature radius of 40 nm was used. The experiments were run in displacement controlled mode due to its sensitivity to transient phenomenon. For this purpose, a miniature capacitive load–displacement transducer was integrated into the TEM holder, which permitting high-resolution measurements of the load–displacement response (resolution of <3 nN in load, <0.02 nm in displacement). Fig. 1(c) shows the dark-field TEM image of the indenter and the carbon coated silicon pillar. Before the in situ nanoindentation test, the cubic diamond tip was carefully adjusted to make sure that the tip can perpendicularly indent on the carbon coated silicon pillar specimen. The nanoindentation tests were conducted at a controlled displacement rate in the range of 2 to 5 nm/s. To investigate the adhesion induced nano-response in the load–displacement curves, two different maximum indentation depths h_{max} (85 nm and 135 nm) were performed on the carbon coating with thickness of 120 nm, which presented the depth smaller and larger than the coating thickness. For coating with thickness of 20 nm, only one depth of 85 nm was chosen to perform the test. The corresponding structural evolution was recorded with a Gatan 830 (SC200) CCD camera.

3. Results

The displacement and load variations with maximum indentation depth of 85 nm on the 120 nm ECR carbon coating were shown in Fig. 2. As shown in Fig. 2(a), during the unloading process, two sudden displacement drops were found and the load decreased to negative values at the same time. The displacement drops implied that the tip experienced from getting rid of contact to re-contact with the sample. Checking the load–displacement curves in Fig. 2(b), it is interesting to note that two re-indentation loops during unloading were detected. For the first re-indentation, the position of the indenter moved a distance, from 33.4 nm to 19.3 nm and to 28.4 nm at last in the very short time, correspondingly, the external loading force (P) applied on the indenter changed from −8.7 μN to 0 μN, and finally to 1.7 μN. The other re-indentation started at indentation depth of 18.1 nm, and the re-indentation load is too small to be clearly observed.

Fig. 3(a)–(f) shows the TEM images during the in situ nanoindentation tests, in one-to-one correspondence with the six points A-F marked in its load–displacement curve displayed in Fig. 2(b). Fig. 3(a) shows the initial aspect before the test. Fig. 3(b) corresponds with the maximum indentation depth h_{max} of 85 nm, where the value of P was 285.4 μN. It could be found that plastic deformation was initiated at the coating surface. At indentation depth of 33.4 nm during unloading (Fig. 3(c)), the loading force exhibited a negative value of −8.7 μN, which was generated by the adhesive force between the tip and the coating. Through Fig. 3(c)–(e), a clear discontinuity in the unloading curve can be observed, and the displacement suddenly dropped followed by moving back. Note that this process took about 0.1 s, in which the external loading force changed from tension to compression as indicated by red dotted arrow in Fig. 2(b) and one loop of re-indentation process occurred. The other re-indentation process started at 18.1 nm of indentation depth, most evident in Fig. 2(a). After complete unloading in this test, a final coating deformation of 20.0 nm was detected from the bright-field TEM image of Fig. 3(f). The whole in situ nanoindentation process was shown from the Supplementary movie M1.AVI.

For the ECR carbon coating with thickness of 120 nm, the other nanoindentation test with the maximum indentation depth h_{max} of 135 nm was performed. The load and displacement versus time are shown in Fig. 4(a), and we can see three displacement sudden drops, correspondingly, the external loading force fluctuated. Fig. 4(b) shows the load–displacement curve, and three obvious re-indentation loops can be found. The re-indentation processes