Nanoindentation Characterization of Single-Crystal Silicon With Oxide Film

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Research Article

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Abstract

In order to obtain ultra-smooth surfaces of single-crystal silicon in ultra-precision machining, an accurate study of the deformation mechanism, mechanical properties, and the effect of oxide film under load is required. The mechanical properties of single-crystal silicon and the phase transition after nanoindentation experiments are investigated by nanoindentation and Raman spectroscopy, respectively. It is found that pop-in events appear in the theoretical elastic domain of single-crystal silicon due to the presence of oxide films, which directly leads the single crystal silicon from the elastic deformation zone into the plastic deformation zone. In addition, the mechanical properties of single-crystal silicon are more accurately measured after it has entered the full plastic deformation.

Introduction

Monocrystalline silicon, as an excellent semiconductor material, is widely used in optical and electronic components due to its excellent performance. The higher engineering requirements in the optical systems of high-precision equipment lead to a focus on improving the surface quality of monocrystalline silicon mirrors. The final removal process for single crystal mirror fabrication is atomic level and therefore machining in the elastic or elastoplastic domain is required. Therefore, the research on the physical and chemical properties of single crystal silicon material is interesting for the manufacture of a single-crystal silicon lens. In particular, its mechanical behavior and deformation mechanism when subjected to external force can provide theoretical guidance for the polishing process of single-crystal silicon.

Recently, nanoindentation has been widely used in the study of nanomechanical behavior of single-crystal silicon. Many studies have been made to research this issue. For example, under certain load conditions, single crystal silicon has undergone a multiphase transition at room temperature[1]. In addition, different loads, holding times and loading/unloading rates played a significant role in determining the phase transition mode of single-crystal silicon[2, 3]. Multiple nanoindentation experiments are performed at the same location of single-crystal silicon, the relative density of the amorphous region remained almost constant, and the volume of the remaining amorphous region formed by the first indentation did not increase[2]. Through molecular dynamics simulation and experimental research on Si (100) nanoindentation, a variety of deformation modes of Si (100) nanoindentation have been discovered, including high-pressure phase transition (HPPT), dislocations, middle cracks, and surface cracks[4]. Further studies have shown that high-pressure phase transition (HPPT) and its mechanical behavior during micro/nano-indentation were closely related to the maximum indentation load, loading/unloading velocity, indenter geometry and the crystal orientation of the sample. Further research shows that the high-pressure phase transition (HPPT) and its mechanical behavior during micro/nano-indentation were closely related to the maximum indentation load, loading/unloading speed, indenter geometry, and crystal orientation of the samples[3, 5]. The scanning electron microscope, microscopy, Raman spectroscopy, and X-ray diffraction have been used to study the phase change of silicon under different loads, and the evolution process of the phase change of the amorphous silicon thin layer is explained[6]. S. Wang et al.[7] studied the phase transition law of single-crystal silicon at

different temperatures. Low temperature has no effect on the production of Si-II during the indentation loading process, but as the temperature decreases, the pop-up phenomenon of monocrystalline silicon is suppressed. The indentation of the cermet (aluminum-silicon) composite material was studied, and it was found that the interface formed a complex dislocation network and increased the fluidity of the dislocation sliding on it, thereby improved the ductility of the composite material[8]. In order to understand the response of single-crystal silicon materials under complex loading conditions, a new limited deformation constitutive model was developed and the accuracy of the model was verified[9]. A nanoindentation study on single crystal silicon deposited with amorphous a-sic ceramic film on the surface was carried out, and the nano-scale elastoplastic response of the film under contact load was systematically characterized and analyzed[10]. However, the research on the influence of surface oxide film to the mechanical properties of single-crystal silicon is rarely mentioned.

In this paper, nanoindentation experiments were carried out on single-crystal silicon with oxide film on the surface. The elastic modulus and hardness of single-crystal silicon (100) were discussed. The change of crystal phase under different load and the pop-in event under low load were described and explained by the imprinting morphology and Raman spectroscopy. In addition, a guideline was obtained for how to accurately measure the precise mechanical properties of materials.

Experiment

Experiments were conducted on the surface of single-crystal silicon. The single-crystal silicon possessed a surface roughness of less than 0.3 nm and surface accuracy of less than 2λ after polishing precisely. After cleaning the single crystal silicon sample with ultrasonic alcohol solution for 30 minutes, take out the sample and evenly select 5 points to be measured on the sample after drying, and then test the thickness of surface oxide film with an ellipsometer (M-2000v) (repeated 5 times). Moreover, four sets of nanoindentation experiments were performed on single-crystal silicon using a Berkovich indenter (Agilent U9820A Nano Indenter G200) at room temperature. The specific experimental parameters are shown in Table 1. (the test should be repeated at least 14 times in each case)

Table 1
Nano-indentation test parameters.

Patterns	Symbols	Pressure	Loading rate(μN/s)	Unloading rate(μN/s)	Maximum displacement(nm)
Static load control mode	A	100μN	10	10	/
	B	150μN	10	10	/
	C	200μN	10	10	/
	D	100mN	10	10	/
	E	200mN	10	10	/
	F	300mN	10	10	/
Continuous stiffness mode	G	/	10	10	1000

After completing the nanoindentation test, the Raman spectroscopy of Renishaw (RM2000) was used to detect the indentation of the sample, which is characterized by the excitation source of the argon laser with a wavelength of 514.5 nm. The output power is limited to less than 100 megawatts to protect the surface from burning effects.

Results And Discussion

3.1 Thickness of oxide film on single-crystal silicon

The thickness of the oxide film on the single-crystal silicon tested by ellipsometer is shown in Fig. 1. Its oxide film thickness has a slight fluctuation at 2.906 nm, which indicates that the oxide film on the surface of the specimen is uniformly distributed. The homogeneous surface helps to improve the accuracy and scientificity of the subsequent nanoindentation test.
3.2 Mechanical properties by nanoindentation experiment

The test principle of nanoindentation on single-crystal silicon is shown in Fig. 2(a). First, the controlled diamond Berkovich indenter gradually approaches the surface of the specimen and enters the single-crystal silicon substrate after passing through the oxide film. Subsequently, the pressure is held at the maximum pressure for 10 s and then leaves the specimen. In addition, in order to determine whether the indenter is worn, the area function of the indenter tip is measured by the continuous stiffness mode of the nanoindentation. The experimental data are shown in Fig. 2(b) and fitted by equation [11]

$$A = c_0 h_c^{2} + c_1 h_c + c_2 h_c^{1/2} + \cdots + c_8 h_c^{1/128} \qquad (1)$$

Here h_c is the contact depth and A is the nominal contact area. c_1 through c_8 are constants to be determined. As shown in Fig. 2(b), when the contact depth is less than 25 nm, the contact area of the indenter can be approximated by the spherical contact area, which can be expressed by Eq. (2). Here R is

the radius of the indenter tip, and the radius of the indenter tip in our case can be obtained from the fitted curve as 230 nm.

$A = 2\pi R h_c$ (2)

However, when the contact depth is deeper than 380 nm, the indenter can be treated as a Bekovich indenter, whose contact area can be expressed as A= 24.11h_c(The contact area of a perfect Bekovich indenter is A= 24.5h_c[11]). In addition, when the contact depth is between these data mentioned above, the contact area of the indenter can be described by $A = 24.11h_c^2 + 1477h_c$, which is a combination of the pyramidal indenter and spherical indenter. It can be found that the tip of the Bekovich indenter indenter is a spherical indenter by the aforementioned results. Therefore, when performing nanoindentation experiments with different parameters, the actual contact area needs to be discussed separately according to the real contact depth[12].

The results of the elasticity modulus and hardness measured in each group of nanoindentation experiments in Table 1 are shown in Fig. 3(a). Experiment groups A-C, namely 100, 150, 200 μN, it is not difficult to find that the elastic modulus and hardness data have large deviations relative to the true values, and large distribution fluctuations are found. In contrast, results with good agreement and small deviations are obtained from the other sets of experimental data. This indicates that the mechanical properties tested in the first three sets of nanoindentation experiments are unstable and less credible compared to the later experiments. Size effect can be used to explain these phenomena, including geometrically necessary dislocations (GNDs) under the indenter tip and inaccurate calculation of contact area[12, 13]. Hence, how can the mechanical properties of the specimens be measured relatively accurately by nanoindentation emerged. Then the elastic modulus under the continuous stiffness mode with displacement of 1μm is analyzed, as shown in Fig. 3(b). And it is found that the elastic modulus of the specimen remained at a stable value only after the specimen entered the full plastic deformation, that is, when the contact depth is greater than 75 nm.

3.3 Pop-in behavior at the interface and effect of stressing

To investigate the effect of oxide film on single-crystal silicon under external forces, the load-displacement curves of the nanoindentation experiment are analyzed, as shown in Fig. 4. Figure 4(a-c) show the load-displacement curves under static loads of 100, 150 and 200 μN, respectively. At the depth of about 3 nm, namely the oxide film thickness, an obvious abrupt change in load is found to appear on the loading curve. Then with the increase of contact depth, the load remains unchanged for a period of time, and finally increases gradually with the increase of contact depth. This is what is referred to in the literature[5–7, 9] as the pop-in phenomenon. In addition, it should be noted that as the maximum static load increases, the amount of abrupt change in load and holding time of its pop-in events increases. This indicates that the larger the applied maximum load is within a certain range, the more obvious the pop-in events is.

However, this is different from the pop-in events recorded in previous literature. The pop-in events is usually found in the plastic deformation zone, accompanied by the pop-out events, as shown in Fig. 4(d). Instead, it appears within the theoretical elastic deformation zone of single-crystal silicon as calculated by Hertzian contact theory[12, 14], which directly leads the single crystal silicon from the elastic deformation zone into the plastic deformation zone. To investigate the reasons for this, the contact stress in the specimen during the nanoindentation experiments are analyzed and the results are shown in Fig. 5. It is found that the contact stress is generally positively correlated with the contact depth until it enters the fully plastic deformation zone, and then remains essentially constant. Nevertheless, it has to be mentioned that from the contact depth of 3 nm, there is a sudden sharp increase in stress and a short-term stress peak is formed. This indicates that stress concentration occurs at interface of the oxide film and substrate, which can be used to explain the appearance of the pop-in events.

3.3 Raman Spectroscopy

To further investigate the cause of the pop-in events, Raman spectroscopy is used to analyze the imprints after the nanoindentation experiment. The Raman results before the experiment and for static maximum loads of 100, 150, and 200 μN are shown in Fig. 6(a). The results show that the Raman spectra of the above experiments have only one Raman peak at 521 cm^{-1}, which is Si-I phase. This indicates that there is no phase transition occurring in the specimen at these cases. The Raman spectra of the continuous stiffness mode with a contact depth of 1μm is shown in Fig. 6(b). In addition to the Si-I phase at 521 cm^{-1} and 310 cm^{-1}, the a-Si phase at 471 cm^{-1} also appears in the spectrum[6, 7]. That is, the phase transition caused by pop-in and pop-out events in Fig. 4(d) occurred in the specimen at this time. At room temperature, the diamond cubic Si-I phase on the surface of single-crystal silicon is transformed into the denser metallic Si-II phase under applied load. Moreover, the Si-II phase will be completely transformed to amorphous silicon (a-Si) at low unloading rates due to its less stable nature[5, 6, 9, 15, 16].

Conclusion

In summary, based on nanoindentation experiments, single-crystalline silicon with an oxide film was tested. It is found that the results are closer to the actual values with less deviation when entering the fully plasticized deformation zone than the data measured under ultra-low load. In addition, pop-in events are found in the theoretical elastic domain of the single-crystal silicon, caused by a stress concentration in the indenter at the interface between the oxide film and the substrate, rather than by the phase transition. Therefore, attention needs to be paid to the influence of oxide films in the ultra-precision processing of single-crystal silicon.

Declarations

Ethics approval and consent to participate

The authors declare that they comply with ethical standards.

Consent for publication

The authors declare that the consent to the publication of the relevant data is granted.

Availability of data and materials

The authors declare that the authenticity of the data and materials used in this paper is guaranteed.

Competing interests

The authors declare that they have no known conflict of interest.

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Authors' contributions

The signed authors have all participated in the work of this paper.

Authors' information

Not applicable.

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Figures

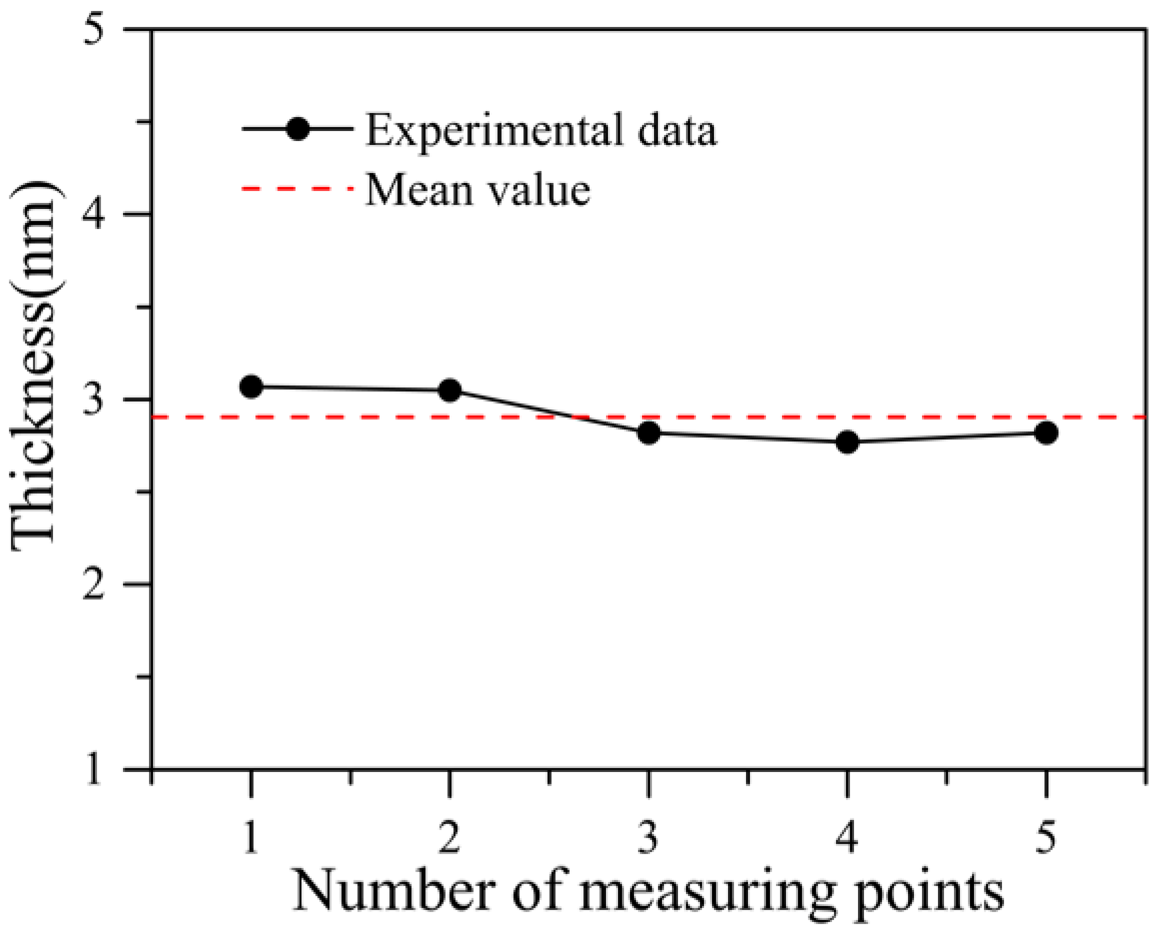

Figure 1

Thickness of oxide film on single-crystal silicon surface

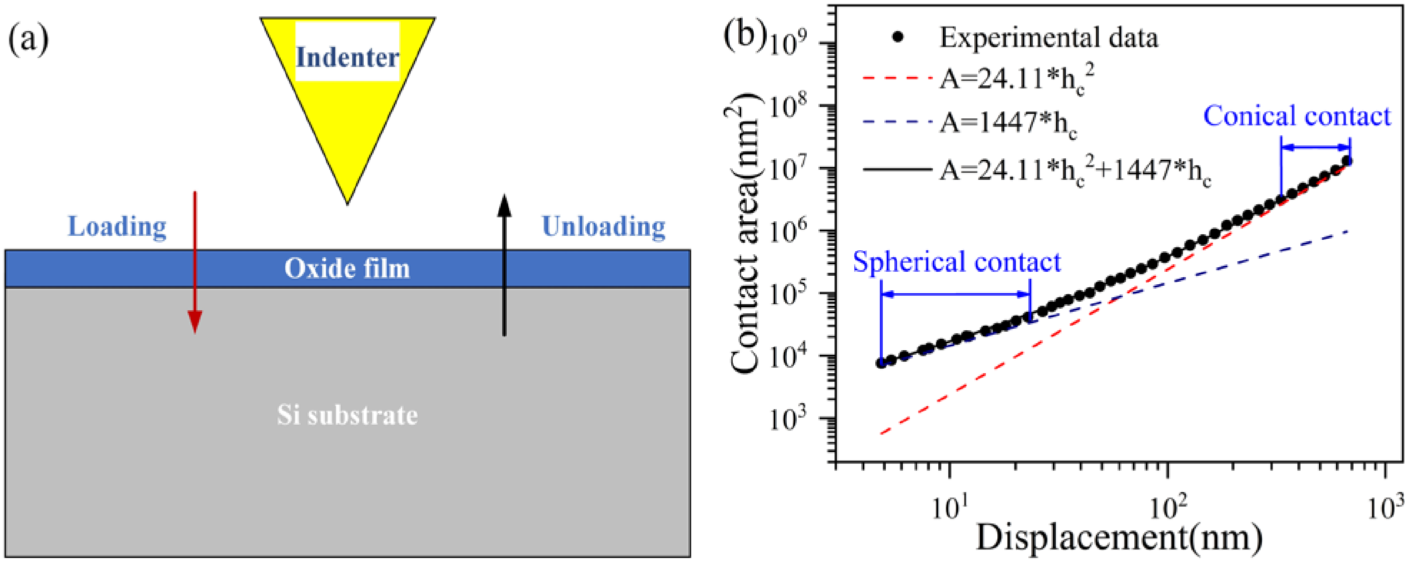

Figure 2

Nanoindentation experiment: a) schematic diagram of the experimental principle; b) fitted graph of contact area

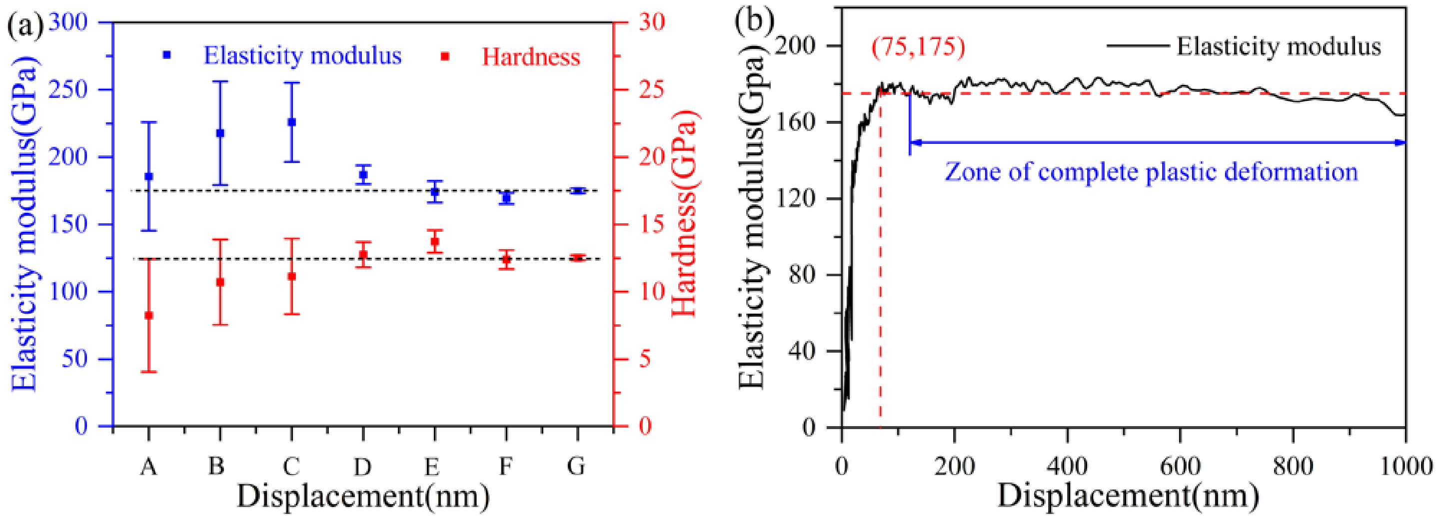

Figure 3

Test data of nanoindentation: a) elasticity modulus and hardness; b) elasticity modulus of the continuous stiffness mode

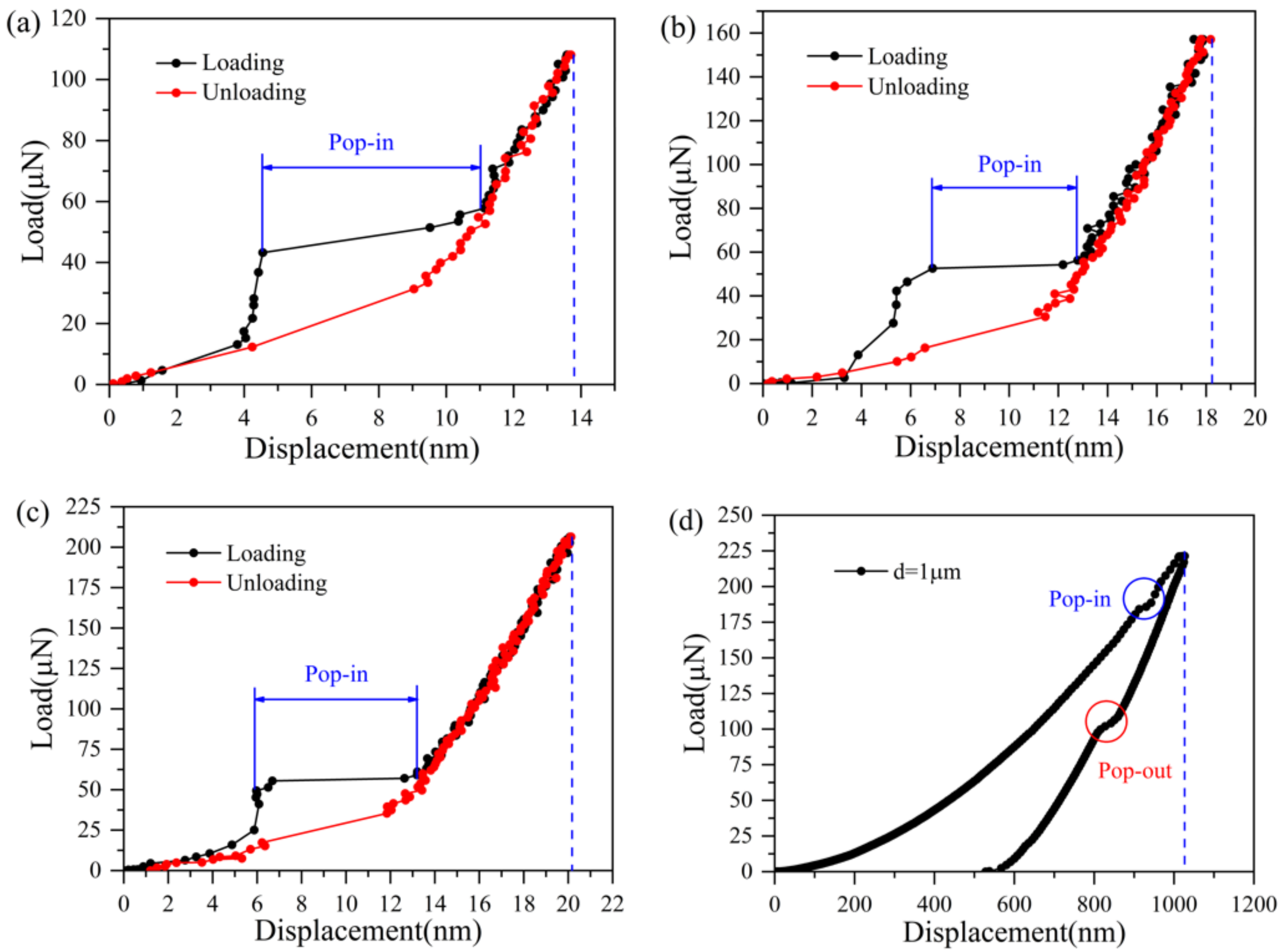

Figure 4

Curve of load with displacement: a) maximum static load of 100 μN; b) maximum static load of 150 μN; c) maximum static load of 200 μN; d) continuous stiffness mode of 1 μm

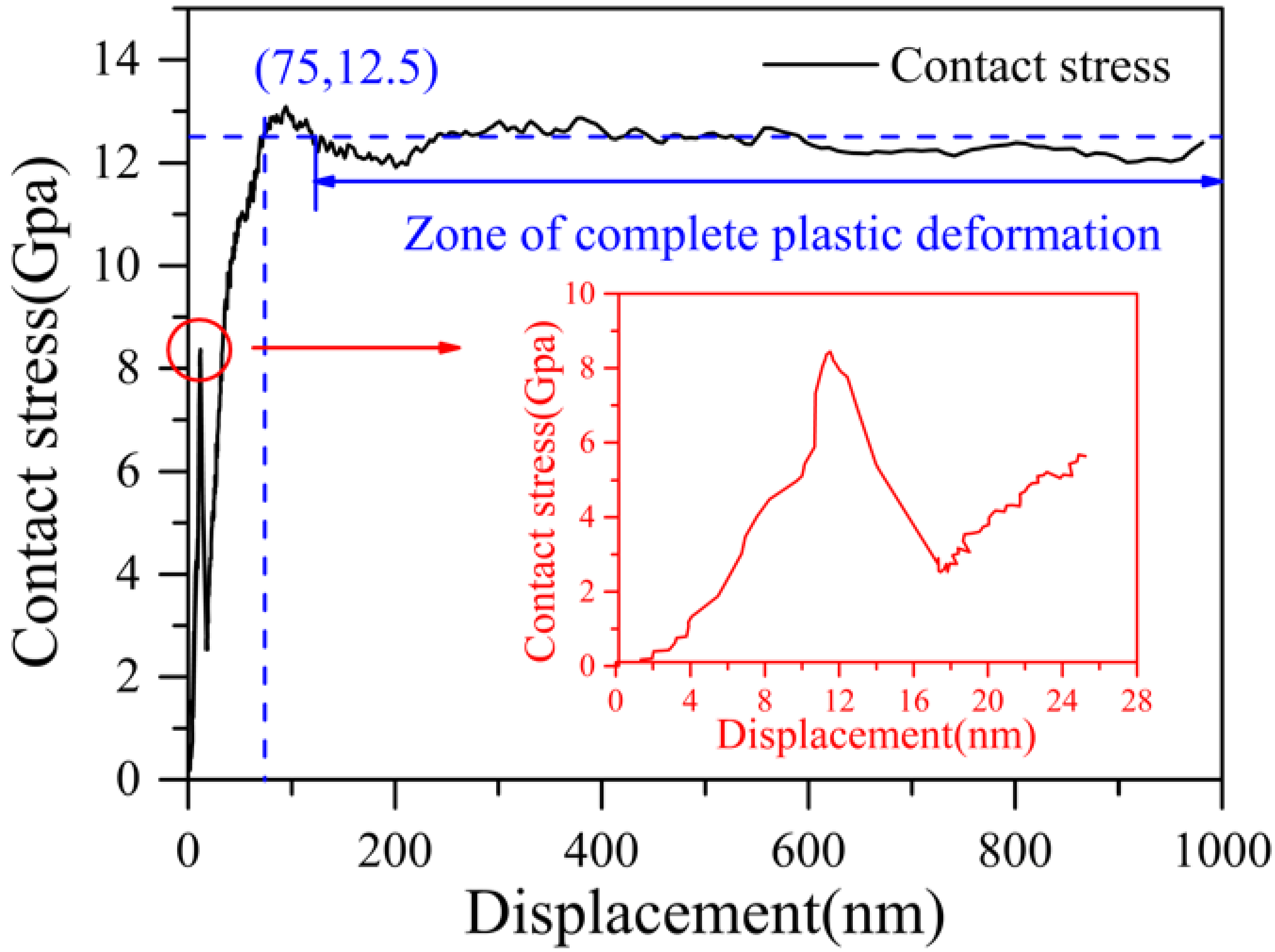

Figure 5

Curve of contact stress versus contact depth

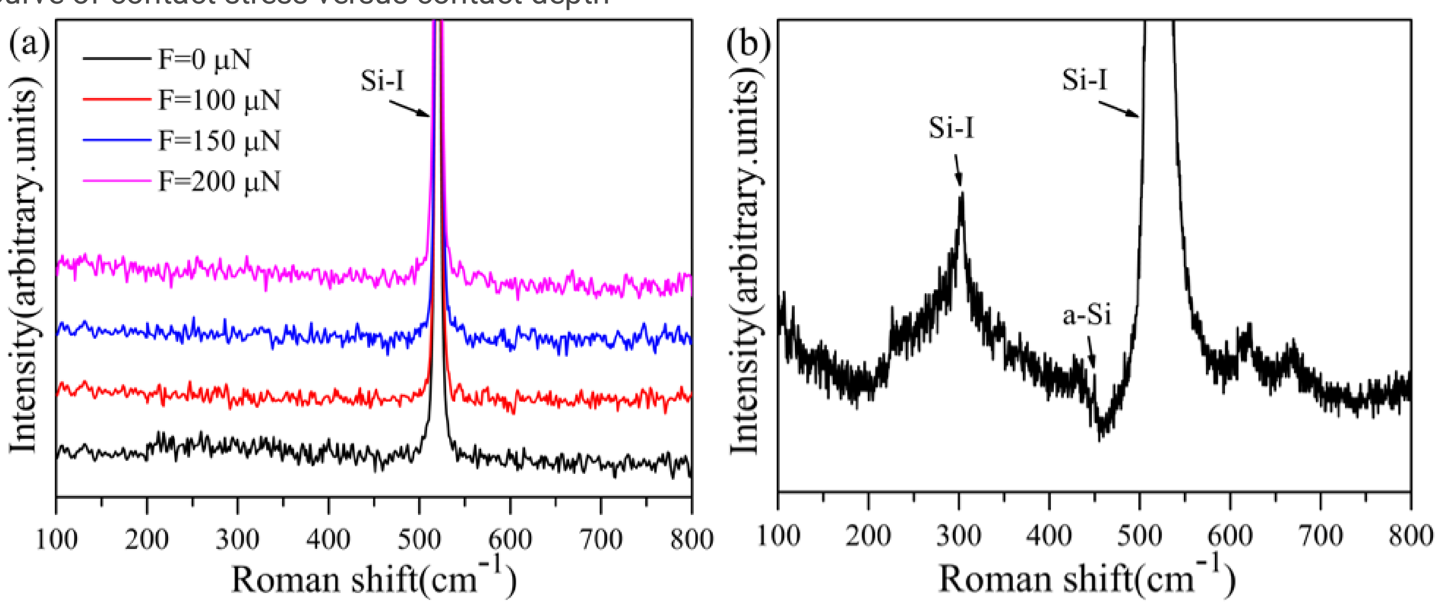

Figure 6

Raman spectroscopy: a) static load control mode; b) continuous stiffness mode