Nanoindentation Characterization of Single-Crystal Silicon with Oxide Film

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Abstract

In order to obtain ultra-smooth surfaces of single-crystal silicon in ultra-precision machining, an intensive 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. The results show that the pop-in event occurring in the theoretical elastic region of single-crystal silicon is caused by the stress concentration at the interface between the oxide film and the substrate. This causes the single-crystal silicon to be converted from the elastic deformation zone to the plastic deformation zone. And at this time, the elastic domain area is almost negligible, which seriously affects the machinability of single-crystal silicon for ultra-precision processing. In addition, the experimental data of single-crystal silicon under ultra-low load deviates greatly relative to the real value and fluctuates widely. However, when the nanoindentation experiment enters the fully plastic deformation zone of single-crystal silicon, the test results of its mechanical properties will be more accurate.

Keywords Single-crystal silicon · Stress concentration · Oxide film · Phase transition · Nanoindentation

1 Introduction

Single-crystal silicon, as an excellent semiconductor material, is widely used in optical and electronic components for its excellent performance. The higher requirements in the optical systems of high-precision equipment lead to a focus on improving the surface quality of single-crystal silicon. The final removal process to fabricate the reflector 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 is interesting for the manufacture of a single-crystal silicon lens. In particular, the 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, multi-phase transitions is occurred on single crystal silicon 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), 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 the 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].
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 amorphous silicon is explained [6]. In addition, S. Wang et al. [7] studied the phase transition law of single-crystal silicon at different temperatures. The results show that low temperature has no effect on Si-II production during indentation loading, but as the temperature decreases, the pop-in phenomenon of monocrystalline silicon is suppressed. The indentation of the cermet (aluminum-silicon) composite material was also 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]. Meanwhile, 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 also discussed. And 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.

2 Experiment

Experiments were conducted on the surface of single-crystal silicon. And 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 min, and 5 points selected evenly to be measured on the sample after drying, and then the thickness of oxide film was tested 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).

After completing the nanoindentation experiments, 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. In addition, the output power is limited to less than 100 MW to protect the surface from burning effects.

3 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. The results showed that the average thickness of the oxide film at the five measured points was 2.906 nm with slight fluctuations, indicating a uniform distribution of the oxide film on the sample surface. 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). The diamond Berkovich indenter first contacts the surface oxide film during the loading process and then enters the single crystal silicon substrate. Subsequently, the pressure is held at the maximum pressure for 20 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].

\[
A = c_0 h_c^2 + c_1 h_c^{1/2} + \cdots + c_8 h_c^{1/128}
\]  

(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, and the radius of the indenter 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 regarded as a standard indenter, whose contact area can be expressed as \(A = 24.11 h_c\) (The contact area of a perfect Bekovich indenter is \(A = 24.5 h_c\) [11]). In addition, when the contact depth is between these data mentioned above, the contact area of the indenter can be described by \(A = 24.11 h_c^2 + 1477 h_c\), which is a combination of the pyramidal indenter and spherical indenter. The aforementioned results show that the actual indenter we used is close to the standard Bekovich indenter and the experimental data is credible. In addition, when conducting 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 elastic modulus and hardness measured in the nanoindentation experiments for each group in Table 1 are shown in Fig. 3(a). Among them, three sets of nanoindentation experiments were selected to investigate the mechanical properties of single-crystal silicon under ultra-low loads according to the actual polishing. Experiment groups A-C, namely 100, 150, 200 \(\mu\)N, it is not difficult to find that the elastic modulus and hardness 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]. Furthermore, there are two main reasons that can be used to explain this phenomenon: 1). There is a drift in the indenter at ultra-low load, which leads to high fluctuations in the results [12, 14]. 2). The displacement at ultra-low load is small and the oxide film accounts for a large percentage, which leads to inaccurate results. Hence, how can the mechanical properties of the specimens be measured relatively accurately by nanoindentation. Then the elastic modulus under the continuous stiffness mode with displacement of 1 \(\mu\)m 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 experiments are analyzed, as shown in Fig. 4. Among them, Fig. 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 as the pop-in phenomenon in the literature [5–7, 9]. In addition, it should be noted that as the maximum static load increases, the load mutation and holding time of the pop-in event will also increase. This indicates that the larger the applied maximum load is within a certain range, the more obvious the pop-in events is. The displacement of the nanoindentation experiment is small under ultra-low load. And in a certain range, the change of displacement is smaller than the change of pressure. That is, the change in contact area is also smaller than the change rate of pressure. As a result, this makes the phenomenon of stress concentration more obvious, and the amount of abrupt change in load and holding time of its pop-in events also increase.

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, 15], which directly introduces the single-crystal silicon from the elastic deformation zone into the plastic deformation zone. This directly shortens the elastic domain of single-crystal silicon to an almost negligible degree, which is extremely detrimental to its elastic domain processing. 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, which is consistent with the location where the pop-in event occurs. This indicates that stress concentration occurs at the interface of the oxide film and substrate, which can be used to explain the appearance of the pop-in events.

### 3.4 Raman Spectroscopy

To further investigate the cause of the pop-in events, Raman spectroscopy is used to analyze the imprints after the nanoindentation experiments. 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. And 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 1 μm 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 occurrence of the pop-in and pop-out events in Fig. 4(d) is accompanied by a phase transition 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 for its less stable [5, 6, 9, 16, 17]. In conclusion, the pop-in event that occurs at ultra-low loads in this paper is mainly caused by the stress concentration at the interface between the oxide film and the substrate [18–20]. The stress release process led to the extension of the displacement and no phase change appeared at this time. In contrast, the phase transition was detected in the Raman test for the imprint under large load, which is the main reason of the pop-in event at this time [6, 12].

### 4 Conclusion

In summary, to investigate the polishable properties of single-crystal silicon under ultra-low loads, single-crystal silicon with oxide films was tested based on nanoindentation experiments. The results show that after entering the fully plastic deformation zone, the test data are closer to the actual values than those measured under ultra-low load, and the deviation is smaller. In addition, pop-in events are found in the theoretical elastic domain of the single-crystal silicon, caused by the stress concentration 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. Necessary measures need to be taken: first, timely anti-oxidation protection is required after each polishing and measurement. Second, minimizing the time that the workpiece is exposed to air during the ultra-precision polishing.
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Declarations

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