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DEVELOPMENT OF NANOINDENTATION TESTER WITH A RAMAN SPECTROSCOPY INTERFACE FOR MATERIAL CHARACTERIZATION

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Abstract – Instrumented indentation test is a simple and effective method for evaluating the mechanical properties such as elasticity/stiffness, hardness and adhesion. During indentation test, materials are subjected to highly localized stresses. It is fundamental interest to explore its mechanical properties under conditions of extreme contact pressure. Raman micro-spectroscopy is a powerful and rapid technique to investigate the pressure-induced phase transformations and the residual stress in the indented region. This technique has been successfully used to study pressure-induced phase transitions of during indentations.

On the other hand, the localized stress during indentation not only causes phase transformation, but also elastic and plastic deformation. The observation of shape of surface or internal material, for example the piling-up or sinking-in behaviour that appears around the indent, plastic zone boundary, the distribution of a lateral crack, and so on, is also important to understand the phenomena during indentation. This understanding also plays an important role in the accurate determination of material properties using nanoindentation test.

In this paper, authors developed the nanoindentation tester with a Raman spectroscopy interface for material characterization. Not only general mechanical properties but also crystalline and residual stress is obtained by this system. The observation data using this system revealed that the stress field around the residual impression.

Keywords: Raman spectroscopy, Residual stress, Surface observation

1. INTRODUCTION

Recently, the necessity of the nanoindentation test for evaluation of mechanical properties such as hardness and Young's modulus in the ultra thin film and the ultra micro area is increases along with the manufacturing and designing of micro devices and the systems. Especially, the necessity for measuring the test piece as it is along with miniaturization of materials is increased, and the grasp of residual stress of the measurement area is very important for material characterization and the improvement of the testing accuracy. During indentation test, materials are subjected to highly localized stresses. It is fundamental interest to explore its mechanical properties under conditions of extreme contact pressure. Raman micro-spectroscopy is a powerful and rapid technique to investigate the pressure-induced phase transformations and the residual stress in the indented region.[1] This technique has been successfully used to study pressure-induced phase transitions of during indentations (e.g Si, Ge[2], diamond[3], and GaN[4]).

On the other hand, the localized stress during indentation not only causes phase transformation, but also elastic and plastic deformation. The observation of shape of surface or internal material, for example the piling-up or sinking-in behaviour that appears around the indent, plastic zone boundary, the distribution of a lateral crack, and so on, is also important to understand the phenomena during indentation. This understanding also plays an important role in the accurate determination of material properties using nanoindentation test.

In this paper, authors develop the nanoindentation tester with a Raman spectroscopy interface by which the residual stress measurement in the micro area by the Raman spectroscopy. Then, authors discuss the influence that the condition in the surrounding include the residual stress exerts for material characterization, and testing accuracy improvement and the validity of the indentation test.

2. THEORY OF RAMAN SPECTROSOCOPY FOR MATERIAL CHARACTERIZATION

2.1. Effect of stress on the Raman modes

Effect of stress on the Raman modes of silicon is reported [5]. Mechanical strain or stress may affect the frequencies of the Raman modes, and lift their degeneracy. One of the first papers addressing theoretically the effect of stress on the Raman modes was that by Ganesan et al. [6] They showed that the frequencies of the three optical modes in the presence of strain, to terms linear in the strain, can be obtained by solving the following secular equation[6,7]:

$$\begin{vmatrix} p\varepsilon_{xx}+q(\varepsilon_{yy}+\varepsilon_{zz})-\lambda & 2r\varepsilon_{xy} \\ 2r\varepsilon_{yx} & p\varepsilon_{yy}+q(\varepsilon_{zz}+\varepsilon_{xx})-\lambda \\ 2r\varepsilon_{zx} & 2r\varepsilon_{zy} \end{vmatrix} \times \begin{vmatrix} 2r\varepsilon_{xz} \\ 2r\varepsilon_{yz} \\ p\varepsilon_{zz}+q(\varepsilon_{xx}+\varepsilon_{yy})-\lambda \end{vmatrix} = 0$$

Here p, q and r are material constants, the so-called phonon deformation potentials, and ε_{ij} are the strain tensor components. The difference between the Raman frequency of each mode in the presence of stress, ω_j (j=1,2,3), and the absence of stress, ω_{j0}, can be calculated from the eigenvalues λ_j:

$\lambda_j = \omega_j^2 - \omega_{j0}^2$ or $\Delta\omega_j = \omega_j - \omega_{j0} = \lambda_j / 2\omega_{j0}$

The polarization direction of each mode, in the presence of stress, is described by corresponding eigenvectors of the secular equation. However, stress obtained in this paper is the total values of all directions.

3. NANOINDENTATION TESTER WITH A RAMAN SPECTROSSOPY INTERFACE

3.1. The overview of the nanoindentation tester with a Raman spectroscopy interface

This system is a nanoindentation tester that can analyze the Raman spectroscopy of the measuring part before and after the indentation test. This device is composed chiefly three parts of Hardness measurement part, Raman spectroscopy analysis part, and the mapping system part. It is thought that the change in the surface properties and the influence of residual stress by the indentation test are distributed complexly in the surface. Therefore, the mapping system in this device is very important. In Figure.1 shows the compositions chart of this system. The optical system for the Raman spectroscopy is taken into the microscope part of indenter, and the view of the Raman spectroscopy must be corresponding to the view of the microscope of the indenter. Moreover, the X-Y stage for the Raman mapping system was built on the X-Y stage for the indenter to do mapping indentation test by not only the mapping observation by Raman spectroscopy. Figure.2 shows the appearance of the nanoindentation tester with a Raman spectroscopy interface. Figure.3 shows the schematic figure of the light path of this system.

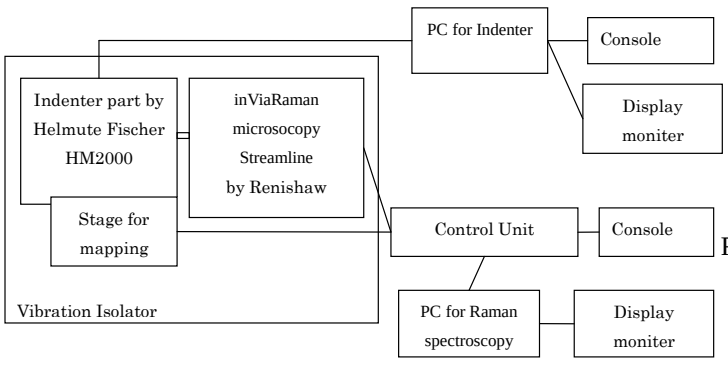

Fig.1 the compositions chart of this system

Fig.2 Appearance of the nanoindentation tester with a Raman spectroscopy interface

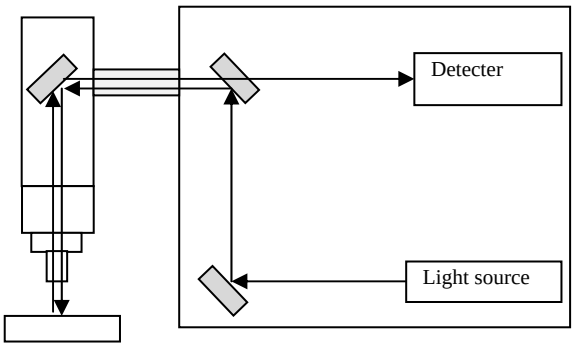

Fig.3 Schematic figure of the light path of the system

3.2. Specifications of the system

In this system, Fischerscope HM2000 made by Helmut Fischer GmbH is adopted as the indenter part, inVia Raman microscope made by Renishaw KK is adopted as the Raman spectroscopy part, X-Y mapping stage made by Renishaw KK is adopted as the Raman mapping system. The specifications of each part is shown as follows,

Indenter part
- Maximum test load: 2000 mN
- Maximum indentation depth: 150 μm
- Load resolution: 0.04 mN or less
- Distance resolution: 100 pm or less
- Approach speed of the indenter: 2 μm/s or less
- Indenter tip: Berkovich, Vickers, Spherical
- The major measuring object:
- Hard material coatings (PVD, CVD), Anodic coatings
- Electroplated coatings, Paint and lacquer coatings
- Synthetics and rubber, Polymeric materials
- Implants, Fiber reinforced plastics and so on.

Raman spectroscopy part
- Raman microscope
- Raman spectrum throughput: over 30 %
- Removal of Rayleigh scattering: 10^{-10} or less
- Incidence efficiency of excitation laser light: over 70 %

Built-in monochromator
Wave number reproducibility: ±0.1 cm^{-1} or less
Resolution of wave number: 2 cm^{-1} or less
Ranges of effective measurement wave number: 200 cm^{-1} to 6000 cm^{-1}
High sensitivity ultra-low noise RenCam CCD detector
Quantum efficiency: over 40% @650 nm
Dynamic range: over 16 bit
CCD element: over 500×300 pixels
Light source for excitation
Oscillation wave length: 532 nm
Output: over 50 mW
Spatial resolution of Raman scattering
Resolution of X-Y plane: 1 mm or less
Resolution of z direction: 2 mm

Raman mapping system part
Spatial resolution: equal to single measurement
Resolution of wave number: equal to single measurement
Measurement area: over 50×50 μm
Ranges of effective measurement wave number: equal to single measurement (200 cm^{-1} to 6000 cm^{-1})

This system supports Renishaw's new StreamLine fast imaging technology, available on inVia Raman microscopes. StreamLine enables users to produce Raman images up to 100× faster than has been possible before; images that used to take hours to produce can now be created in minutes. Generally laser point scans the surface of test piece to produce the Raman mapping images. But in this procedure, line shape laser scans the surface to produce the images quickly.

3.3. Expected roles of this system

This system is able to analyze the Raman spectrum before and after the indentation. Therefore, the applications to the material that has crystal structure, thin film material that needs to evaluate adhesion with substrate and electric device material that changes physical properties by stress are expected. Measurement cases observed by this system will be introduced in the next chapter.

4. MEASUREMENT CASES BY NANOINDENTATION TESTER WITH A RAMAN SPECTROSCOPY INTERFACE

Some measurement cases are introduced in this chapter. Silicon wafer is used as the test piece, because it is well-known sample of Raman spectroscopy and indentation test. Investigations about strain determination on silicon surface by Raman spectroscopy are reported [8, 9]. In the next section, the Raman mapping observation after the indentation test is introduced. Also the measurement case by the approach of both indentation test and Raman mapping is introduced in 4.2.

4.1. Raman mapping observation after the indentation test

Silicon wafer was indented with 2.0 μm maximum indentation depth. In this test condition, indentation loads are around 735 mN. We made several sets of indentations on the surface on the test piece. After the indentation test, Raman spectra have been acquired at room temperature using Raman mapping system. Mapping area is 60×60 μm, it is enough to observe the residual impression and surface around it.

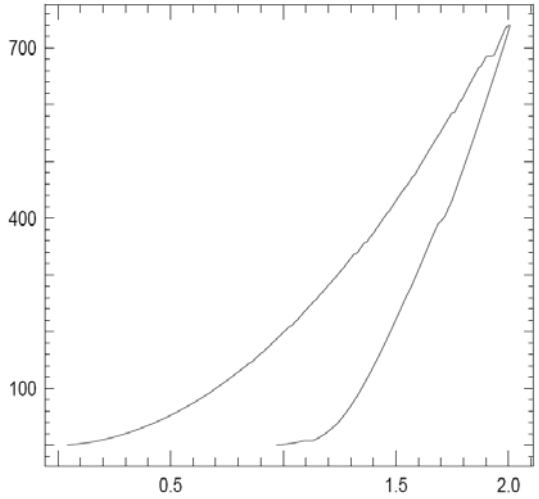

Fig.4 P-h curve of indentation test

Indentation test was carried out with mentioned test condition. P-h curve is shown in Fig.4. From the test results, we obtain quite constant values close to 6400 N/mm^2 at the Martens hardness and 141 GPa at the modulus. Optical image of indented Si surface is shown in Fig.5. From this optical image, there are no cracks generated around the imprint. The crack might influence the stress field around imprint. The similar observation at the higher load will be discussed in the future.

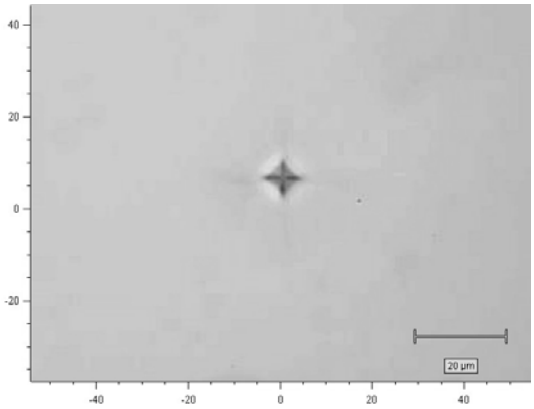

Fig.5 Optical image of indented Si surface

Raman mapping observation was carried after the indentation test. Peak position image around the residual impression is shown in Fig.6. From this observation, we obtain the clear stress field around the impression. This field is extended very widely. Generally, distance between the

individual hardness test is three times and more of the size of residual impression. However, this Raman mapping image shows more long distance is needed in this test piece. This kind of observation is very useful to precise indentation test without the influence of residual stress. In the future work, it is necessary to understand what influence the size of stress field. And we will elucidate the direction of stress by using ellipsometry determination.

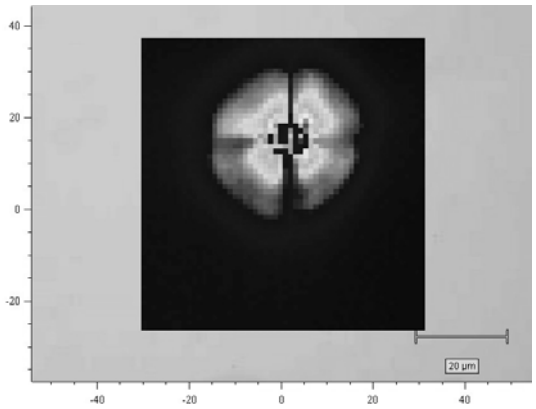

Fig.6 Raman mapping image around residual impression

4.2. Approach of both indentation test and Raman mapping

Figure 7 is the measurement case by the approach of both indentation test and Raman mapping. This figure shows the relationships between Martens hardness and Raman spectra around the large residual impression with the test load 20 N. Raman mapping image is shown in Fig.8. Generally, it is known well that the residual stress influence the rise of hardness. But in this case, many cracks and dislocations are generated around the imprint. It is thought a cause of decrease in hardness. From these measurement cases, the utility of this nanoindentation tester with a Raman spectroscopy interface for material characterization was confirmed.

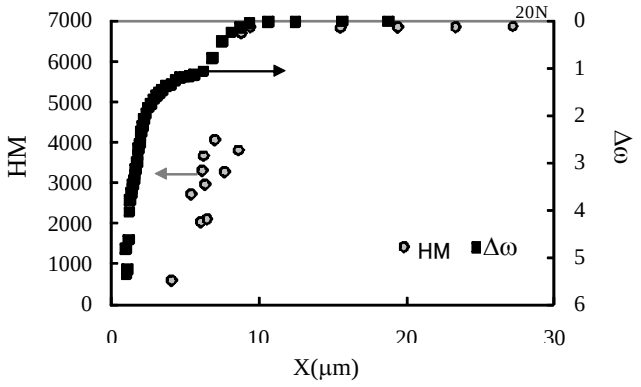

Fig.7 Relationships between Martens hardness and Raman spectra around the large residual impression

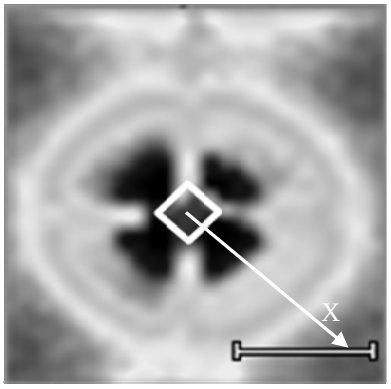

Fig.8 Raman mapping image around the residual impression with the test load 20 N

4. CONCLUSIONS

In this work, authors focused the Raman spectroscopy to observe the stress and crystalline of the surface of test piece. The nanoindentation tester with a Raman spectroscopy interface was developed, and the following conclusions were obtained.

1) The Raman spectroscopy is a very useful technique to obtain the stress and crystalline of the test piece. However, the material that doesn't have Raman activity cannot be measure.

2) The nanoindentation tester with a Raman spectroscopy interface for material characterization is developed and utility of this system is confirmed.

3) It is necessary to understand what influence the size of stress field. And we will elucidate the direction of stress by using ellipsometry determination.

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