

Microindentation device for *in situ* study of pressure-induced phase transformations

Yury Gogotsi,^{a)} Thomas Miletich, Michael Gardner, and Michael Rosenberg
Department of Mechanical Engineering, University of Illinois at Chicago, Chicago, Illinois 60607

(Received 7 April 1999; accepted for publication 15 September 1999)

In situ microscopic and spectroscopic studies of samples allow us to understand the mechanisms and measure kinetics of phase transformations in materials. We use a light microscope and a Raman microspectrometer to study phase transformations induced by contact loading. Many interesting phenomena occur in materials during indentation that can only be analyzed during indentation, *in situ*. By analyzing what occurs to ceramics and semiconductors *in situ* we can gain valuable insight into the mechanisms and kinetics of phase transformation. A microindentation device has been designed and fabricated to achieve these objectives. The microindentation device can provide the means to study pressure-induced phase transformations in real time. The basic design of the device is adaptable to several configurations, so that the device may be used in a wide variety of applications. The device consists of a piezoelectric actuator (piezoelectric translator), load cell, linear microscrew stage, translation stage containing the specimen mount and specimen holder, and diamond-tip indenter. For the first time, an indentation tester has been coupled with a Raman microspectrometer to conduct *in situ* studies of pressure-induced phase transformations. This article describes the design, operation, and experimentation of a microindentation device for the *in situ* analysis of pressure-induced phase transformations in materials. © 1999 American Institute of Physics. [S0034-6748(99)04412-3]

I. INTRODUCTION

Pressure-induced phase transformations have been studied for years using various high-pressure cells. The progress in this field depends strongly on the development of new technologies and instrumentation. Improvement of anvil construction allowed researchers to achieve higher and higher pressures and led ultimately to high-pressure diamond synthesis and discovery of many new high-pressure phases.¹ A major breakthrough in high-pressure research was achieved with the introduction of diamond-anvil cells (DAC) which allow for *in situ* studies of phase transformations at pressures exceeding 1 Mbar.² Our recent, successful use of the combination of indentation and Raman microscopy³⁻⁶ led to a new leap in studies of pressure-induced phase transformations due to the simplicity and efficiency of this technique. Its ability to drive shear-induced phase transformations that would only occur at higher pressures, as well as its relevance to industrial processes such as machining and hardness testing, make it a valuable item. However, the experiments described in our first publication⁴ were conducted on samples after application of the contact load. High-pressure phases which could not survive depressurization were not realized due to the limitations of the available technology. Inability to monitor the indentation process *in situ* also limited our ability to characterize the exact transformation route and the sequence of phases formed during pressurization and decompression. To solve this problem, we used a simple screw-driven device^{3,5,6} which allowed studies on transparent

materials such as quartz and diamond, however, this device did not allow measurement of the applied load or indentation depth. Thus, it could not be used to determine phase transformation pressures, the manual loading process did not allow for any control over loading and unloading rates, which can strongly affect the outcome of the experiment.⁴ A more sophisticated and precise manual screw-driven device described in Ref. 7 had similar limitations.

For indentation tests, hardness testers (Vickers, Brinell, Rockwell, and others) are utilized. A variety of indenters can be used to drive phase transformations (Fig. 1). For these indenters, stress calculations have been conducted and the equations for calculating hardness values can be found in the literature.⁸ The indenter types can be substituted for the purpose of studying the effect of shear/compressive stress ratios, which are determined by indenter shape, on phase transformation. For this purpose, low-cost cone-shaped indenters with different angles can be as effectively used. Eventually, it is anticipated that an indenter with a flat end could be used, as well.

A microhardness tester can also be coupled with a microscope. However, in a classical configuration, we cannot simultaneously utilize the indenter and the objective. In this configuration, we are forced to focus on an area on the material which we would like to indent. Then the indenter is set into position. Once the indentation is complete, the objective is repositioned so that optical measurement can be taken. Thus, with the available technology we are impeded. During the indentation process, it is not possible to see the indentation site nor perform any Raman measurements.

To accommodate this quandary, it became necessary to

^{a)}Electronic mail: ygogotsi@uic.edu

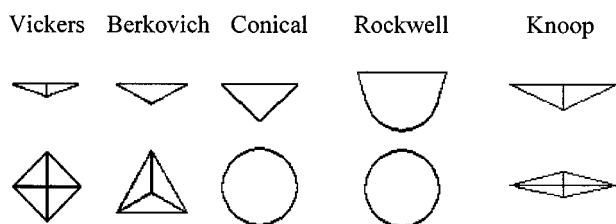


FIG. 1. Various diamond indenter tips that may be used by the microindentation device (not to scale).

design a device for *in situ* indentation/Raman studies of pressure-induced phase transformations.

Special loading devices have been available for simultaneous (*in situ*) tests. There exist a number of devices, both commercial and noncommercial, for bending and other mechanical tests under a microscope, (e.g., Kamrath and Weiss).⁹ However, these devices do not allow us to perform hardness indentation tests. Additionally, most of them have been designed for special types of microscopes and loading conditions that do not satisfy requirements for study of phase transformations.

A very limited amount of work has been done in the field of *in situ* indentation analysis. Particularly in the field of transmission electron microscopy (TEM), work done by Wall and Dahmen¹⁰ has led to their design of a nanoindentation specimen holder used for observing the evolution of the microstructure located directly underneath the indenter as it strikes the silicon specimen. The microstructure is viewed *in situ* in cross section using a high-voltage TEM. Their system is designed for nanoindentation and the indenter is moved rather coarsely with a gear motor drive until it is within ± 0.5 mm of the silicon specimen. At that point, the specimen holder with its silicon sample is inserted into the electron microscope. Once a desired area is chosen for indentation, the indenter tip is positioned until it appears close to the desired indentation area. At this point, the alignment of the indenter tip along the direction of the electron beam must be achieved. With these steps being taken, the analysis of the microstructure underneath the indenter as it indents the sample ranging from 10 to 100 nm indentations can be achieved *in situ*.

This device works in the range of nanoindentations, whereas for Raman microanalysis an area of $1 \mu\text{m}^2$ or larger is required. An additional requirement for Raman spectroscopy study is the variability of the incident angle for the laser beam, whereas the indenter must always be positioned orthogonally to the sample surface.

Another indentation device was designed for use with a scanning electron microscope.¹¹ This device used flat, blunt, indenters to push single fibers out of a composite material with the purpose of measuring the interfacial strength in composites. Thus, it was designed for a different purpose and for use under different conditions and with different indenters.

None of these indentation devices have ever been coupled with a Raman microspectrometer. Although a diamond indenter assembly, which occupies one microscope objective position, is commercially available from Leica, it

does not allow simultaneous Raman analysis and indentation. A Renishaw Raman microspectrometer was coupled with a scratch tester,¹² but again, Raman analysis was done subsequent to scratch tests.

Thus, a device is needed which will allow indentation under the microscope while simultaneously monitoring the phase transformation process by Raman spectroscopy. This need has been addressed and represents the scope of work upon which this article is based.

II. DESIGN AND OPERATION OF MICROINDENTATION DEVICE

A. Design of the microindentation device (MID)

The goal of this design effort is to develop and manufacture a computer-controlled device that would permit indentation of our test specimens from several different positions while simultaneously taking Raman measurements from above. Such a device necessitated the following:

(i) An indenter positioned orthogonally to a mount on which we can place our specimen, also to be orthogonal to the indenter, so that we indent our specimen perpendicularly.

(ii) The ability to rotate the loading device, with the indenter still orthogonal to the mount, so that we can take Raman measurements at a variety of positions on the face of the specimen. It is also necessary to have the capacity to analyze the material that "squeezes out" from between the surface of the specimen and the indenter.

We needed a simple, reliable and nonexpensive device for indentation tests that can be used with a light microscope. The requirements of the design were the following:

- (i) height/width: < 50 mm;
- (ii) material of the device frame: stainless steel or cemented carbide;
- (iii) material of indenter: diamond;
- (iv) working temperature: -200 – 30 °C;
- (v) force: up to 100 N;
- (vi) observation of both viewing directions (side and bottom of the sample) must be possible during indentation into varied sample types;
- (vii) two-dimensional positioning of the sample must be possible;
- (viii) angle change from 0° to 90° must be possible;
- (ix) the indenter must be controllable in its translational motion and loading; and
- (x) direct force and displacement measurement.

The requisite indentation procedures that needed to be accomplished with the microindentation device (MID) consisted of four different scenarios (Fig. 2):

(A) Performing a vertical indentation of a transparent material from beneath and focusing the laser through this material from above, onto the indenter tip.

(B) Performing multiangle indentations on nontransparent material and focusing the laser on the material which "squeezes out" around the indenter tip.

(C) Performing a horizontal indentation of a transparent material and focusing the laser through this material, onto the indenter tip or material which squeezes out around the indenter tip.

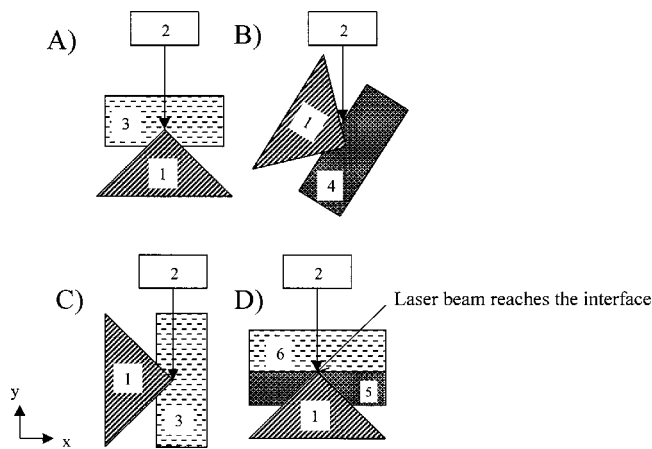


FIG. 2. Four scenarios of performing indentation analysis: (A) The micro-indentation device (1) rests vertically while the laser beam coming through the microscope objective (2) is focused through a transparent material (3). The indenting is performed in the y direction. (B) The microindentation device is positioned under a 45° angle while the laser is focused on the tip of the indenter where material has squeezed out of a nontransparent sample (4). (C) The microindentation device rests horizontally while the laser is focused through a transparent material. (D) A thin coating (5) is placed on a hard transparent substrate (e.g., sapphire) (6) and the laser is focused through the substrate to scan the material of interest.

(D) Performing a vertical indentation [similar to case (A)] on a thin film of material which is positioned between the indenter tip and a clear and transparent substrate. The laser is focused through the substrate and onto the backside of the indented material.

When considering the design constraints inherent to the system, it is clear that for such a device, small-scale parts are necessary due to the fact that the entire MID must be able to rest on a microscope stage without interfering with the microscope objectives. In addition, not only must the device be able to rest horizontally on the microscope stage, it also must be able to be oriented at different angles so that optimal Raman laser scanning can be achieved. The MID was designed for use with a Renishaw 2000 Raman microspectrometer, equipped with a Leica DM LM/P type 20 microscope. However, it can be used with most metallographic microscopes and other Raman microspectrometers. The components selected for the MID all satisfy the size and cost con-

straints along with the needed precision operation. The components are as follows: (1) linear translation stage with micro-screw (for coarse positioning); (2) piezoelectric translator (PZT) (for fine positioning and indentation); (3) load cell (for registration of load measurements); (4) specimen stage (containing the specimen mount and specimen holder); and (5) diamond-tip indenter (Figs. 3 and 4).

Through the in-concert utilization of Raman microspectroscopy and the MID, along with a computer program to control the operation of the device in a closed-loop system (Fig. 5), the reality of *in situ* phase transformation analysis can be achieved. Any changes or alterations encountered during operation would be diagnosed and reconciled during the operation via the software program, e.g., no pause or system shut down would be experienced.

B. Operation of the MID

The MID consists of a diamond-tip indenter, load cell, PZT, and linear translation stage with micro-screw. All of these components are housed in a metal frame which is attached to the translation stage, along with the specimen mount and holder (Fig. 4). The space constraints under the microscope have been accounted for so that the MID can rest on the microscope stage beneath them and experiments can be carried out without conflict.

The micro-screw slide is used for coarse, manual positioning of the indenter. Once the indenter is just touching the test specimen, set screws are tightened and the system is ready to perform a hardness test. At this time, the PZT is activated via the control software to provide fine, micropositioning (e.g., indentation). As the diamond tip penetrates the material, the load cell concurrently measures the applied force. The data gathered during the indentation process (rates of loading or unloading, force applied to specimen, etc.) are processed through a data acquisition system consisting of a variable channel multiplexer, a multifunction module, and data acquisition control software in a closed-loop system (Fig. 5).

Upon assembly of the MID it was observed, through experimentation, that the linear micro-screw stage was spring loaded. The micro-screw stage assembly would actually be

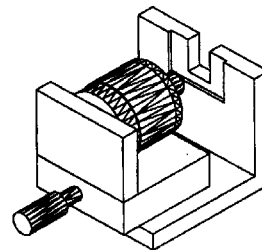
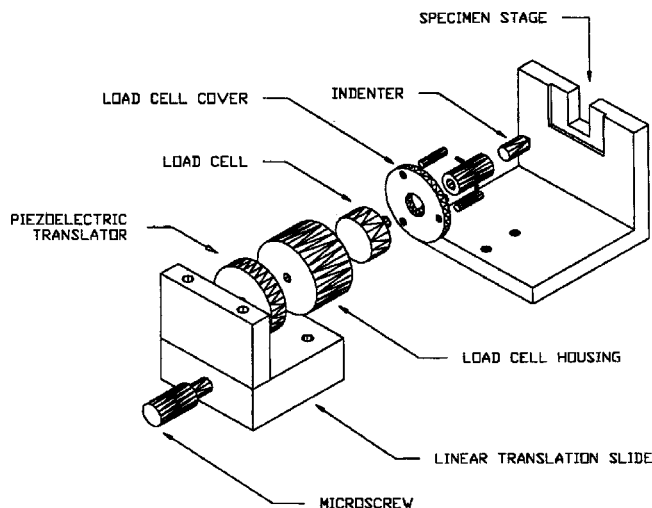


FIG. 3. As indicated by the figure on the left, the microindentation device consists of several miniature components, each with its own responsibility in the functioning of the device. Once assembled, the microindenter is shown on the right.

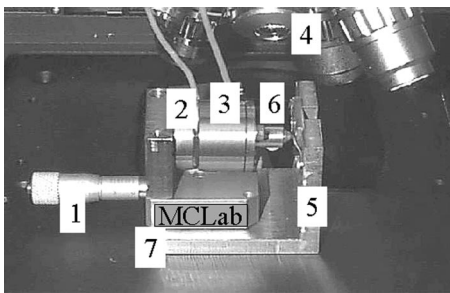


FIG. 4. The microindentation device: (1) micro screw, (2) piezoelectric translator, (3) load cell, (4) microscope objectives, (5) specimen stage, (6) indenter, and (7) linear translation stage.

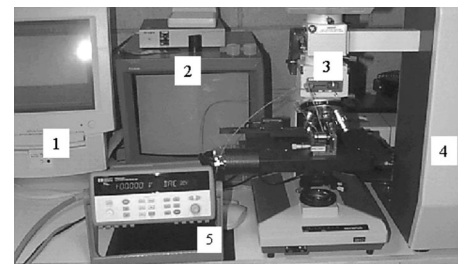


FIG. 6. Microindentation device and the data acquisition system, with the video and computer monitors in the background: (1) control computer monitor, (2) video camera monitor, (3) microscope, (4) spectrometer, and (5) data acquisition system.

‘pushed back’ as the indenter struck the specimen. This phenomenon was not accounted for in the original design. Only during experimentation was the importance of this behavior realized. Therefore, additional work was performed on the device in the following manner:

- (i) A slot was cut and counterbored on the bottom side of the translation stage.
- (ii) The diameter of the slot matched the diameter of the hole in the upper corner of the micro screw stage.

(iii) The slot was cut in such a way to where it lined up with the micro screw hole.

(iv) The length of the slot was equal to the full range of motion of the indenter.

(v) A screw can be used to secure the micro screw stage, and all of its attached components, to the translation stage once it is determined that the indenter is just touching the material, at which time the PZT will be activated.

The following quantities can be monitored for any specimen:

(i) Loading rate: expressed in terms of mm/s or N/s, this quantity specifies that rate at which the material is being forced by the indenter.

(ii) Maximum load: this quantity specifies the upper limit that will be acquired with respect to load.

(iii) Holding time: once the maximum load has been achieved, this quantity specifies the time duration that the indenter will remain at that chosen maximum load.

(iv) Unloading rate: this quantity specifies the rate at which the indenter should be retracted from the specimen.

By experimenting with different values of the above parameters, we can study phase transformations in hard materials or thin films of materials on hard substrates, as schematically shown in Fig. 2.

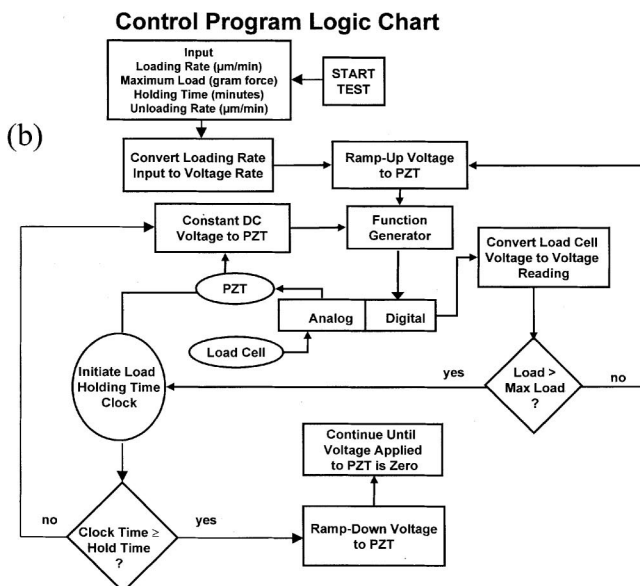
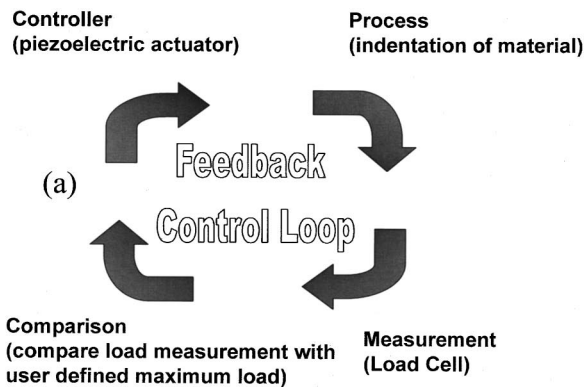


FIG. 5. (a) Microindentation device feedback control loop and (b) HP-VEE program logic diagram.

III. EXPERIMENTAL VERIFICATION AND RESULTS

We used diamond cones sharpened to a point (90° angle, Lunzer) to produce the indentations. The experimental system based on a Renishaw 2000 Raman microspectrometer and an Olympus BU 2 microscope is shown in Fig. 6.

A. Nontransparent material

Silicon was used as an example of a nontransparent material. Multiangle indentations [configuration (B) in Fig. 2] were performed on silicon where the ‘squeezed-out’ material was analyzed. Previous studies have revealed that silicon undergoes a phase transformation under the pressure of diamond-tip indenters.⁴ This phase transformation is to a ductile, metallic state (Herzfeld–Mott transition). Furthermore, this phase transformation can be detected through Raman microspectroscopy. While Raman microspectroscopy is hardly able to detect the actual metallic phases of silicon in this test configuration, it is able to detect the change to the metallic phase when it occurs as well as phases that occur

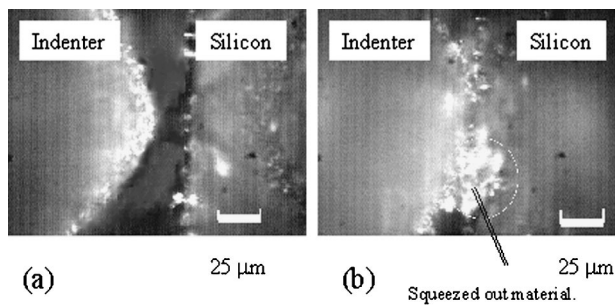


FIG. 7. (a) Microindenter device just prior to indentation. The conical indenter is on the left-hand side. The sample is in the center, and a reflection is visible on the right. (b) Microindenter device during indentation. Note the material squeezed out.

during or after unloading. It has been suggested that the ability to perform *in situ* measurements of a material while it is being indented could allow for a much greater understanding into pressure-induced phase transformations.³⁻⁵ Figure 7(a) shows the indenter before it strikes the specimen sample. Figure 7(b) shows the sample material which has squeezed out as a result of the indentation process. This material which squeezes out is the area of interest for micro-Raman spectroscopy. The results of these Raman scans can be seen in Fig. 8. All Raman scans were performed at a magnification level of 500 \times with the spot size of about 2 μm in diameter. The specimen was a (100) silicon wafer. As Fig. 8 demonstrates, there is clear evidence of phase transformations, namely, evidence of amorphous Si, producing broad bands at approximately 470 and 150 cm^{-1} . Hexagonal Si-IV is indicated by the peak at 506 cm^{-1} as well as metastable Si-XII (*r8*) bands at 169 and 354 cm^{-1} and Si-III (*bc8*) bands were also found (not shown in Fig. 8). Note in the lower spectrum the presence of hexagonal silicon is not accompanied by any other alternate phases of silicon. This shows, as was earlier postulated, that hexagonal silicon can be created due to twinning of cubic Si-I without transformation to metallic Si-II. On the other hand, amorphous Si-I, Si-III, and Si-XII are expected to be formed through a metallic β -Sn phase.^{3,4}

These Raman spectra show that this microindenter

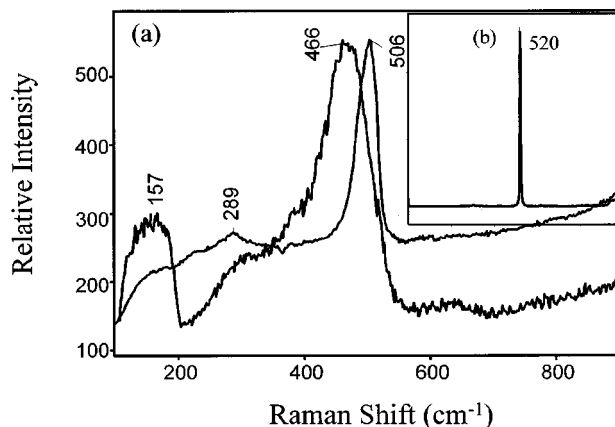


FIG. 8. (a) Spectra of material squeezed out from between the silicon chip and the indenter. The peaks at about 470 and 150 cm^{-1} correspond to amorphous silicon and the peak at 506 cm^{-1} corresponds to hexagonal silicon. (b) Pristine silicon prior to indentation.

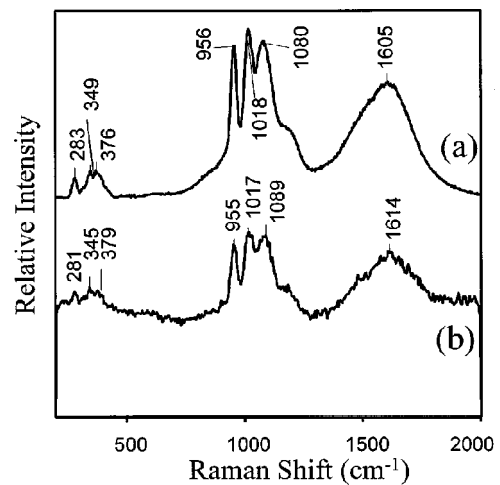


FIG. 9. (a) Spectrum of pristine cubic zirconia. (b) Spectrum of indented cubic zirconia.

device is capable of producing phase transformations in semiconductors when incorporating the multiangle indentation scenario. It also confirmed that the material which squeezed out of the indentation was ductile and the debris around the indenter was not the result of brittle indentation-induced fracture of Si.

B. Transparent materials

Another material experimented with was transparent cubic zirconia stabilized with Y_2O_3 . It is known that cubic zirconia does not transform to a monoclinic phase under indentation. This experiment was conducted in configuration (A) (Fig. 2) to prove that the spectral changes observed in other materials are due to indentation-induced phase transformations. Figure 9 shows Raman spectra of the cubic zirconia before and after indentation. The upper spectrum obtained in Fig. 9(a) corresponds to nonindented cubic zirconia. Once indented, the area around the indenter tip was focused upon with the Raman laser. The spectra obtained are shown in Fig. 9(b). There is no significant change in the Raman spectrum of this material during indentation except for a minor peak shift due to stress.

Indentation on diamond was conducted in the test configuration shown in Figs. 2(a) and 2(c). We used the (111) surface of a large, synthetic diamond crystal (a yellow synthetic diamond from Russia). *In situ* microscopy observations of the indentation process (Fig. 10) demonstrated that diamond becomes nontransparent to visible light, that is, the entire area shows the reflection of the light in the indentation area. This is in agreement with closing the optical window in diamond which was discovered under very high hydrostatic pressure.¹³ The indenter tip became flat after testing, due to the extreme hardness of the (111) diamond surface. Although the interaction zone and the material squeezed out could be analyzed in all configurations shown in Figs. 2(a), 2(b), and 2(c) (see Ref. 6 for details), *in situ* analysis through diamond as shown in Figs. 2(a) and 2(c) was hindered by the luminescence of diamond under stress. This problem is known for diamond anvils, and a special choice of diamond crystals

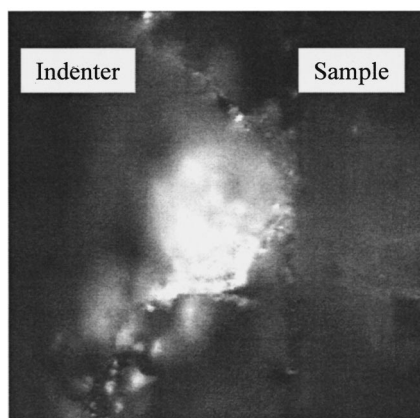


FIG. 10. Optical micrograph of a diamond indenter in contact with the (111) surface of a large diamond crystal. Light area at the indenter tip is the phase transformation zone.

which do not produce a high-luminescence background under loading is required to obtain significant spectra. In our case, all Raman bands except the major band of cubic diamond disappeared under the very intense background spectrum.

IV. CONCLUSIONS, FUTURE CONSIDERATIONS, AND POTENTIAL APPLICATIONS

The designed device was successfully used to perform indentation/Raman tests on hard materials and enabled studies of indentation-induced phase transformations. This device can also be coupled with a Fourier transform infrared microspectrometer in reflectance mode to study phase transformation in IR-active materials. However, further improvement of the device is certainly possible. For example, a capacitance displacement gauge can be used to measure displacement of the indenter with a higher accuracy. The device can also be better integrated with the Raman spectrometer. In particular, GRAMS 32 spectral software that is used to control the Renishaw Raman spectrometer can also be used to control the device through the same computer window. This would serve not only to eliminate an additional computer that is currently utilized, but also compare the Raman spectra with the load-displacement curve in real time.

In recent years, Raman microspectroscopy has been used to measure surface stresses in crystalline solids by monitoring the modulations of Raman frequencies with externally applied loads.¹⁴ The microindentation device allows for *in situ* studies of stress fields around indenters; this can help to check experimentally a large amount of theoretical work conducted to date.¹⁵ An additional benefit of the designed system is that if the indenter were to be replaced by a cylindrical loading roll, it can be used for three-point bending tests of miniature bars. We hope to be able to closely monitor the stresses on a sample and gain an insight into fracture

mechanics that has not been previously available. The system will use the same housing and drive equipment; the major change will be to the indentation device. The indenter will be replaced with a flat rounded tip. Also, a protective plate needs to be installed on the rear of the device to eliminate any chance of damage to the microscope being used. Furthermore, bending tests can be used to calibrate the Raman system for stress analysis, since the tensile stress on the surface of a bent bar can be easily calculated.¹⁶

The miniaturization of electronic components and development of microelectromechanical systems (MEMS) are revolutionizing modern industrial products. New methods of micromachining are required to improve the machining quality and spatial resolution. Additionally, mechanical testing and quality control of MEMS and MEMS materials is only possible under a microscope because of their small size. The designed device can be used for mechanical testing of MEMS and materials for MEMS, when properties must be determined on a microscale. Other important applications of the designed device can be envisioned.

ACKNOWLEDGMENTS

The authors would like to acknowledge the undergraduate senior design team of the Department of Mechanical Engineering, UIC, whose efforts led to an initial design of our current device: Brenda Teaster, Walter Ludwig, Steve Kaszonyi, and Benjamin Escobar. The authors would also like to thank Sung Lee of the Department of Electrical Engineering and Computer Science, UIC, for his assistance to this project. This work was supported by NSF Grant No. DMI-9813257 and by Motorola through the UIC Manufacturing Research Center.

¹R. M. Hasen, *The New Alchemists* (Times Books, New York, 1993).

²H. K. Mao and R. J. Hemley, *High Press. Res.* **14**, 257 (1996).

³Y. G. Gogotsi, A. Kailer, and K. G. Nickel, *Mater. Res. Innovations* **1**, 3 (1997).

⁴A. Kailer, Y. G. Gogotsi, and K. G. Nickel, *J. Appl. Phys.* **81**, 3057 (1997).

⁵Y. G. Gogotsi, M. S. Rosenberg, A. Kailer, and K. G. Nickel, in *Proceedings of the Workshop on Tribology Issues and Opportunities in MEMS*, edited by B. Bhushan (Kluwer, Dordrecht, 1998), pp. 431–442.

⁶Y. G. Gogotsi, A. Kailer, and K. G. Nickel, *J. Appl. Phys.* **84**, 1299 (1998).

⁷A. Kailer, Ph.D. dissertation, Eberhard-Karls-Universität, Tübingen (1998).

⁸I. J. McColm, *Ceramic Hardness* (Plenum, New York, 1990).

⁹Kammrath and Weiss, Germany, Company Newsletter (1997).

¹⁰M. A. Wall and U. Dahmen, *Microsc. Res. Tech.* **42**, 248 (1998).

¹¹J. Janczak, G. Burki, and L. Rohr, *Key Eng. Mater.* **127**, 623 (1997).

¹²Raman Scratch Tester, CSEM, Switzerland, Company Newsletter (1997), (<http://www.csem.ch/instrum>).

¹³A. L. Ruoff, H. Luo, C. Vanderborgh, and Y. K. Vohra, *J. Appl. Phys.* **69**, 6413 (1991).

¹⁴E. Anastassakis and E. Liarokapis, *J. Appl. Phys.* **62**, 3346 (1987).

¹⁵A. E. Giannakopoulos and P.-L. Larsson, *Mech. Mater.* **25**, 1 (1997).

¹⁶J. M. Gere and S. P. Timoshenko, *Mechanics of Materials*, 4th ed. (PWS, Boston, 1997).