In-situ Raman mapping during indentation

I I Maslenikov and A S Useinov

Technological Institute for Superhard and Novel Carbon Materials, Troitsk, Moscow, 142190, Russia
i.i.maslenikov@gmail.ru

Abstract. Transparent diamond tip described elsewhere allows combining mechanical indentation measurement with optical methods, including not only surface observation, but also spectroscopy measurements, in particular, Raman spectroscopy. Current work considers the possibilities of creating Raman maps, which give an information about the pressure distribution and ratio of material phases. Corresponding maps are presented for the case of indentation of DLC film on a silicon sample.

1. Introduction

Transparent diamond tip was invented for the instrumented indentation tester “NanoScan-4D” – a device that conducts a measurement of hardness and elastic modulus by means of instrumented indentation [1]. In contrast with traditional indentation, this method relies on force-displacement data, rather than force and direct area values, which allows conducting measurements faster and with a smaller depth. However, on the other hand, the method neglects a “pile-up” and “sink-in” effects, which are taken into account when direct optical imprint area observation is used. The transparent tip allows observing the sample’s surface in the real-time regime: before, during, and after the indentation, which allows measuring the imprint area without additional movement of the sample to the optical microscope. Thus, a direct imprint observation becomes faster and the area defined by means of instrumented indentation can be corrected with optical image for “pile-up” effects.

Naturally, the transparent tip can be used not only for the residual imprint area measurements, but also for the location of indentation, measurement of surface deformation and crack propagation during the scratch and, which is probably more straightforward, for the spectroscopy measurement. In order to be more consistent in description of corresponding measurement, one must take into account the tip shape. A detailed explanation is presented in Ref. [2], a concise description can be given as follows. A diamond cylinder is faceted in the way that its both ends have the Berkovich-pyramid shape. Pyramids’ heights are parallel to each other and lie along the same line. Pyramids are symmetrical with respect to the indenter’s centre so that each face of a given pyramid has a parallel face on the opposite end. Described configuration of the faces allows each incident beam of light that propagates parallel to the pyramid’s height and falls into the indenter in the vicinity of the tip to go through the indenter and propagate parallel to the previous direction with a shift in the perpendicular direction only. The shift value as well as the visible area size are dependent on the indenter’s height [2].

Therefore, each image directly observed through the tip consists of three sectors and the connected picture can be obtained via their simple linear translation. All maps in the following sections are presented for only one sector, the rest parts of the image differ only due to the indenters manufacturing shortcomings.
The ability of the tip to transmit the light can be used to combine mechanical and spectroscopy measurements [3]. Similar simultaneous opto-mechanical measurements were known before, however, they didn’t make use of the light passing through the tip. Work [4] considers an indentation of the transparent sample when spectra are collected from the bottom side of the sample, work [5] describes an indentation near the sample’s edge with the collection of spectra in perpendicular direction. Current approach, which is described in [3], isn’t limited to near-edge indentation and can be used for the opaque samples.

2. Experiment conditions
Raman mapping was performed using specially designed unit [3], that fits into the Renishaw InVia Raman spectroscope and allows applying the load by means of the stepper motor actuator and measuring the force acting on the indenter by means of the load cell. A silicon covered with a ~200 nm thick DLC coating was chosen as a sample for investigation. An indentation was performed up to the force of 40 N with further unloading up to the force of 30 N. When the load was achieved, the spectra were collected. A 514 nm laser, 3000 l/mm grating, and 20x objective were used. In the first experiment, five spectra were collected along the one of visible sectors diagonal, these points are shown in the Figure 1. Collection time was 60 s, each spectrum was collected five times and then averaged. In the second experiment, mapping over the visible sector’s area was performed, the map contains 28x25 pts with 10 μm interpoint step. In each point 30 spectra were collected and averaged. Each spectrum had an acquisition time of 2 seconds. Optical image of the surface after the full unloading presented in the Figure 1b was obtained with the help of Sensofar S NEOX optical microscope in multicolour regime by stitching multiple captures in-focus regions.

3. Results
Figure 1a represents points of spectra collected in the first experiment, the picture was taken at the load of 30 N, after the unloading from 40 N load. In this sector, one can see black points in the left bottom corner, which correspond to the more evident debris seen in the Figure 1b, after the unloading. This picture also shows a number of cracks that occur mostly during the unloading cycle of the indentation. The section of Figure 1b, corresponding to the section visible in the Figure 1a is highlighted with yellow lines.

Figure 2b shows an example of spectrum collected during the mapping at the point 6 (Fig. 1a). This spectrum shows three peaks, which correspond to diamond (1332 cm$^{-1}$), DLC (1420 cm$^{-1}$), and Si-I (520 cm$^{-1}$). Spectra collected at the points 1-5 are shown in the Figure 2a. The detected frequencies are 50-900 cm$^{-1}$, that range was chosen to resolve peaks corresponding to the different phases of Si. The
Figure 2. (a) The low-frequency spectra with the silicon phases peaks obtained at the points “1” to “5”. (b) A full range spectrum obtained as a part of the mapping.

spectra are quite similar to the results presented in Ref. [3]. Each of them has an intensive peak that corresponds to Si-I phase (520 cm\(^{-1}\)). The range of intensities is limited to 20000 to underline the evidence of weaker peaks that correspond to the different phases. However, we can tell that, as it is partially seen from the Figure 2b, the most intensive peak 520 cm\(^{-1}\) corresponds to the point “3”, then intensities descend in the following order “2”, “1”, “4”, and “5”. Such behaviour can be most likely attributed to the following factors. Points “1” and “2” are located in the regions, where DLC coating is still present on the surface, points “4” and “5” are located in the region, where silicon bears a load and, since the unloading has already partially occurred, this silicon is transformed to different phases. Point “3” is located right at the edge of the indent – in the region where DLC coating is cracked and is likely to be at least partially chipped out, while uncovered silicon bears small load and thus significant part of the signal corresponds to the Si-I phase. Consideration presented above can be used to the explanation of the largest 520 cm\(^{-1}\) peak intensity at the point “3”. The peaks in the range below 520 cm\(^{-1}\) can be attributed to Si phases as it is done in the work [3]. Peaks at 181 and 300 cm\(^{-1}\) correspond to the a-Si, a peak at 161 cm\(^{-1}\) corresponds to Si-III phase, while a “pile” around ~390 cm\(^{-1}\) corresponds to the mixture of Si-III and Si-II phases [3].

Obtained spectra can be used for the properties mapping. Using the shift of the centre of the DLC line, one can obtain the pressure map. In order to obtain the corresponding picture, each spectrum was approximated by a fifth power polynomial in the range of frequencies from 1380 to 1600 cm\(^{-1}\), then the argument of the fitted line maximum was used as a value that corresponds to the local pressure. Obtained map is shown on the Figure 3a. As can be seen from the picture the maximum pressure is observed in the contact region, in particular below the pyramid edges. Another feature seen on the figure is the low pressure in the sector centre, which can be attributed to the delamination of the DLC from the silicon.

Figure 3. (a) Distribution of pressure (by the DLC-peak frequency). (b) Si-I to DLC peaks intensities ratio map.
Figure 4. Intensities ratio $I(340-410 \text{ cm}^{-1})/I(510-545 \text{ cm}^{-1})$ map.

Another example of the map, which represents the ratio of Si-I to DLC is shown in the Figure 3b. The map was obtained by dividing the maximum intensity within the range 510-540 cm$^{-1}$ to the maximum intensity within the range 1400-1460 cm$^{-1}$. The picture has a peak that is likely to be caused by the chipped Si crumbs lying over the DLC surface.

The map showing the ratio of maximum intensity within 340–410 cm$^{-1}$ to the maximum intensity within 510–545 cm$^{-1}$ frequency range is shown in the Figure 4. That map can be qualitatively and roughly attributed to the amount of Si-I transformed to the different phases. The map has a background level of 0.06 that corresponds to the case when there are no observable peaks within 340–410 cm$^{-1}$ range. Regions near the sector’s edges are excluded from the picture as they have either a very small Si-I peak or no peaks within 340–410 cm$^{-1}$ range. Thus, these near-edge areas have phases ratio value about 0.6, which is highly caused by artefacts and, therefore, is inappropriate.

4. Conclusions
Presented results show the possibility to conduct an in-situ Raman mapping during the indentation measurements. It has been shown that combining mechanical testing with optical structure investigation is useful for local material characterisation. These methods implemented in a single instrument can be particularly useful for the heterogeneous materials and the materials that undergo the phase transformations.

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