Micro Raman Spectroscopy as a Powerful Technique to Analyze Structural Phase Transitions of Silicon Crystals

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Abstract. In this work a study on silicon undergone structural phase transitions by two different methods were performed. The samples were submitted to high non-hydrostatic pressure applied by cyclic Vickers indentations. The indentations were performed on virgin surface (polished as received) and on an amorphous surface generated either by the diamond turning process or RF sputtering. The analysis on the machined surface, debris on the diamond tool and around of imprints were also performed using micro Raman spectroscopy.

Introduction

Silicon is well known, at normal atmospheric conditions, to present cubic diamond structure, labeled Si-I. Under a combination of high temperature and hydrostatic pressure (by using diamond anvil cell, for example), it may assume up to eleven different structural phases depending on the decompression rate [1]. Microindentation is a simple alternative route to produce, into and around the imprint, these structural transformations. In the present paper we report the effect of the initial state of silicon surface on the formation of the different structural phases. We used crystalline samples, completely amorphous grown by RF sputtering and partially amorphous produced by single point diamond turning in ductile regime. The microchips left on the tool rake face and the surface structure modifications were probed by means of Raman micro spectroscopy .

Experimental Details

The specimens were in the form of squares (10 x 10 mm) cut from silicon wafers (100) 1-10 Ω.cm type p (B – 10^{15}-10^{16} atoms/cm^3) of 55 mm diameter and 500 μm thick with surface orientation. The amorphous Si (a-Si) films were prepared by radio frequency (13.56 MHz) sputtering a polycrystalline silicon target in an atmosphere of pure argon. The films, typically 1 μm thick, were grown onto microscope slides kept at approx. 175 °C during deposition. The Raman measurements are performed using a T64000 Jobin-Yvon micro spectrometer, using the 487.9 nm line of an argon ion laser. The laser power was kept low at about 0.5 mW, in order to avoid heating effects, an important care to be considered for analyzing highly disordered samples.

Results and Discussions

Figure 1 shows a sequence of non-indented, 1, 5 and 10 indentation cycles of crystalline Si. From the first to the fifth indentation cycle (Fig.1b and 1c) the only effect is the generation of an amorphous phase (a-Si), along with the crystalline phase (a-Si +c-Si), denounced by the broad band at 470 cm-1, preserving however the peak at 521 cm^{-1}, due to the Si-I, in the diamond cubic structure. The formation of a multiple phases state with several different structural phases is only produced after 7 cyclic indentations, as displayed in Fig.1d (the best spectrum obtained after 10 cycles). In the Raman spectrum can be identified the following peaks: at 165, 353, 398 cm^{-1} from Si-XII; 175, 386, 440, 490 cm^{-1}, Si-III; 182 cm^{-1} from Si-XIII (?); and at 495 cm^{-1} from Si-IV [1]. Figure 2 shows a sequence of Raman spectra of non-indented, 10 and 15 indentation cycles of the completely amorphous Si sample, prepared by RF sputtering. Although the experimental methodology employed was exactly the same as that in the crystalline sample, it is clear from the resulting Raman spectra that any crystalline phase was formed. This may be indicative that is not possible to generate crystalline phases from the amorphous bulk only applying pressure, that is, the pressure induced transformation from Si-IX, Si-IV, Si-XIII to a-Si is irreversible. Figure 3 shows the sequence of Raman spectra of non-indented, 1, 3, 10 and 15 indentation cycles of the partially amorphous machined sample. Contrary to the case of c-Si where the Raman peak at 521 cm^{-1} due to the Si-I is recovered after some a few cycles, in the machined sample this peak is not recovered completely, even after 15 cycles. It seems easier to produce Si-XII and Si-III than Si-I from the partially amorphous phase. In the case of these partially amorphous samples, there are two assumptions to explain the multiple phase formation: i) as it is formed by nanometric crystallites immersed in an amorphous matrix [2-3], it is possible that these metastable phases are nucleated from these crystallites [2-4, 5], and/or ii) as the partially amorphous layer is on a crystalline substrate, the multiple phase grows from it [5]. For both possibilities, an important matter to be considered is the fact that the metastable phases of silicon are, in reality, distortions of the original cubic diamond structure. In order to illustrate the effect of the structural phase transformations induced by the machining process in the ductile regime, Figure 4 displays a Raman spectrum of silicon debris left on the tool surface with several metastable phases already identified in the microindented samples (Fig. 2and Fig.3).

Conclusion

Summarizing, we performed a Raman scattering study of the effect of the initial morphology of the silicon surface on the non-hydrostatic pressure induced structural phase transformation. For all tested samples, prepared by different methods, micro Raman spectroscopy showed that this technique can be considered a powerfull technique to evaluate physical modifications of materials induced by mechanical forces.

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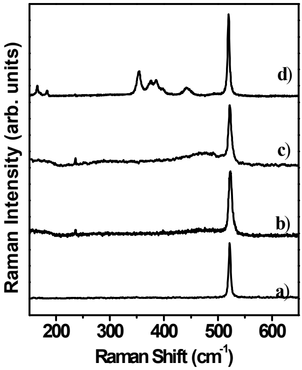

Fig. 1- Right: Raman spectra of crystalline Si indented with 15 mN load for a) non-indented, b) one cycle, c) five cycles and d) ten cycles.

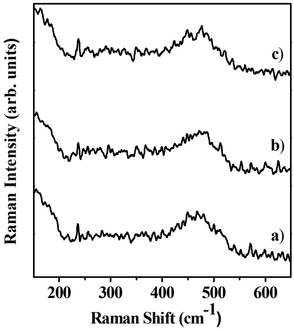

Fig. 2- Raman spectra of completely amorphous Si, indented with 15 mN for a) non-indented, b) 10 cycles and c) 15 cycles.

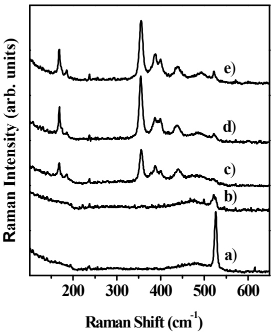

Fig. 3- Raman spectra of partially amorphous Si, obtained by RF sputtering, indented with 15 mN load for a) non-indented, b) 1 cycle, c) 3 cycles, d) 10 cycles and e) 15 cycles.

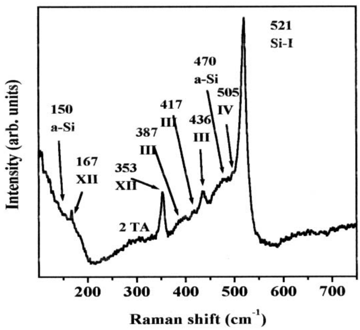

Fig. 4- Raman spectrum of a Si debris on the diamond tool after machining Si surface in the ductile regime, showing the formation of several structural phases induced by the pressure applied by the tool tip on the Si surface.