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Microscopic and spectroscopic investigation of phase evolution within static and dynamic indentations in single-crystal silicon

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ABSTRACT

Silicon undergoes multiple phase transformations during indentation, and its final phase depends primarily upon the rate of unloading. In this study, single-crystal silicon was subjected to static and dynamic indentations in order to evaluate the propensity for particular phase transformations as a function of unloading strain rate. Raman spectroscopy and transmission electron microscopy were employed to map the phase distribution within and beneath the indent impression. It was found that silicon behavior is strongly dependent on unloading strain rate, with the preferred final phase switching from crystalline polytypes to nanocrystalline Si. The manuscript provides data in the intermediate strain rate range (10^3–10^5 s^{-1}) that is not currently available in literature and links published nanoindentation to shock testing results, crucial to predicting material response at a range of strain rates.

1. Introduction

Silicon (Si) is the ubiquitous semiconductor, used for wafers, metal-oxide-semiconductor field-effect transistors, substrates, and in photovoltaics. These applications require extensive processing of the silicon, usually under high-velocity cutting processes such as machining, dicing, lapping, and scribing [1–5]. Under quasi-static loading, it is well-established that the dominant deformation mechanism of Si is phase transformation, which is dependent upon a number of variables including pressure, temperature, and unloading rate. Compared with data cataloging Si behavior at quasi-static strain rates, information concerning silicon response under moderate strain-rate loading at high pressures (such as in lapping and polishing) is minimal. Further, rapid, high-pressure testing (e.g., shock testing) indicates that the prominent phase transformation differs from that under quasi-static loading [6], but no analyses linking these two extreme loading conditions have been attempted. Through the use of dynamic indentation testing, this research evaluated Si response at moderate strain rates in order to complete the continuum of material response between quasi-static and shock testing strain rates. Traditional indentation tests are conducted at quasi-static strain rates (10^{-2} s^{-1}) and do not capture material response at high strain rates. Dynamic indentation testing [7] adapts the indentation testing method to higher strain rates, and the current study is the first to report dynamic indentation (10^3 s^{-1}) test results of single-crystal silicon. This technique has previously been used to assess the dynamic properties of a variety of metals [8], ceramics [9], glasses [10], and metallic glasses [11].

The primary deformation mechanism of silicon under high-pressure loading is phase transformation, though cracking and dislocations are also observed [12,13]. Multiple publications have detailed the sequence of phase transformations during loading and unloading of indentation [14–17], and only a brief summary is provided here. The typical cubic diamond structure of virgin silicon (Si-I) transforms to a metallic β-Sn structure (Si-II) under pressures ranging from 8.5 to 13 GPa [17–19]. Transformation from Si-I to Si-II during the loading phase has been confirmed with in-situ x-ray diffraction and Raman spectroscopy [15,18] and through a notable decrease in resistivity [19,20]. The hardness of Si is approximately the same as the pressure required for the Si-I to Si-II phase transformation (8–12 GPa [20–23]), and thus Si-II is the only high-pressure phase typically reached during indent loading. However, diamond anvil cell (DAC) testing has subjected Si to 248 GPa of pressure, and several additional polytypes were noted to form at higher pressures, including orthorhombic, hexagonal, and face-centered-cubic (FCC) structures [24,25].

The newly-formed, high-pressure Si-II phase is unstable under low pressure, and it undergoes additional transformations to new phases during unloading [17]. The phase transformation process upon pressure release is quite complex, but a simple dichotomy of phase evolution has been proposed: formation of either 1) disordered or amorphous phase or 2) new crystalline polytypes. Amorphous silicon (a-Si) tends to form under blunter indenter tips

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(i.e., lower pressure), lower loads, and faster unload rates (insufficient time for crystalline phase nucleation [14,26,27]). Slower unloading leads to the formation of rhombohedral (R8 or Si-XII) and body-centered cubic (Si-III or BC8) phases [14]. Si-XII is formed first and then transforms to Si-III with decreasing pressure [1,18,28]. A mixture of the two crystalline phases (Si-XII and Si-III) is generally noted at ambient pressure [29,30]. This simple dichotomy is not definite; many indenter shapes and unload rates have produced both amorphous and crystalline phases, and a hexagonal wurtzite structure of Si (Si-IV) may also be present, further complicating phase analyses. Si-IV can result from annealing of Si-III phase [31] or possibly from shear deformation of the diamond cubic crystal lattice in shock loading [17]. Other transitional phases such as Si-XIII and Si-IX [32] also exist, but they are unstable, typically not found in the indentation imprint, and thus are not discussed here. This unloading process requires particular attention because the final Si phase may drastically impact overall performance. Si exhibits multiple properties that are phase-dependent: 1) electrical conductivity is greater for the more metallic Si-III/Si-XII versus a-Si [15,33] and less for Si-III than Si-IV [24,34], 2) amorphous Si has slightly lower hardness than Si-I [35] and 3) residual stress could be different depending on the final phase formed, e.g., residual stress in Si-III is 11% larger than Si-I [36]. Therefore, gaining increased understanding of Si response to pressure and unloading rate is of critical importance.

As seen in the preceding paragraphs, the majority of the experimental research has focused on phase transformations beneath nano- and microindentations of various geometries, including spherical, Berkovich, Vickers, and Knoop, all with relatively slow unloading rates (10^{-5}–10^{-3} s^{-1}). The few moderate-strain-rate range tests such as machining [3,4] and scratch testing [5] have noted amorphous and crystalline phases in Si wafers. At the far end of the rate spectrum, shock loading of single-crystal Si up to 60 GPa [37] has also been performed to study phase transformations under dynamic, high-pressure conditions, leading to data with unloading strain rates on the order of 10^6–10^9 s^{-1}. Depending on crystal orientation, the Hugoniot elastic limit, (HEL), of Si ranges from approximately 5.5 [38,39] to 9 GPa [39,40]. Below the HEL, the material remains elastic, but when subjected to shock pressures over the HEL, silicon experiences an elastic wave followed by a phase transformation wave at a pressure of approximately 13.5 GPa [37,41]. Based on the simple phase dichotomy described earlier, the final Si phase after unloading may be expected to be a-Si because of the rapid unload rates associated with shock testing. However, after shock testing, the impacted region was not amorphized as would be expected based on unloading rate [14] but instead displayed a transition to polycrystalline silicon (Si-I) from the initial single-crystal diamond cubic phase [6]. A small volume of Si-III/Si-XII phases at lower pressures (11 GPa) has also been noted [6]. Thus, there is a noticeable difference in the deformation mechanism between indentation (predominantly amorphous and single-crystal phases other than Si-I) and shock testing (nanocrystalline Si-I). Further, DAC testing at high pressures has not produced this nanocrystalline Si phase, hinting that the final phase is rate- as well as pressure-dependent. Dynamic indentation experiments [7], described in the Section 2, provide data at high pressures and intermediate strain rates and are deemed a crucial bridge between nanoindentation and shock wave testing.

Post-testing, Si phases are identified through x-ray diffraction [18], Raman spectroscopy [1,16,17,42–44] and transmission electron microscopy (TEM) [16,20,26,45,46]. Of these characterization techniques, micro Raman spectroscopy has submicron spatial resolution and is ideal for creating maps of phase distributions within an indented region. Further, Raman spectra are distinctly different for the different phases of silicon, as seen in Fig. 1. Si-I has

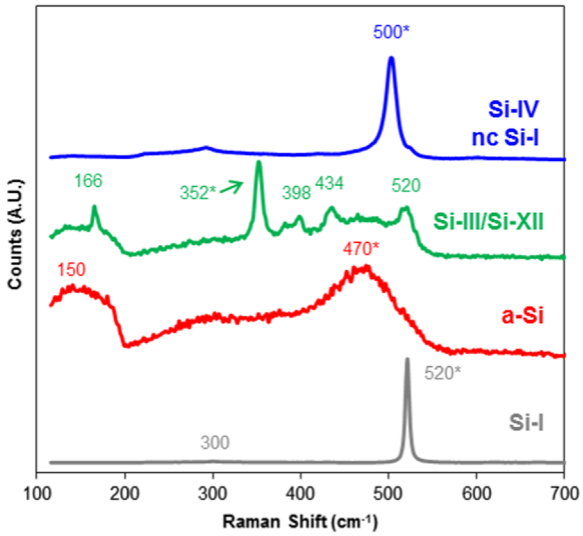

Fig. 1. Raman spectra of Si phases typically located within an indentation. Peaks marked with an asterisk (*) were used for phase identification and creation of phase maps.

an intense, sharp peak around 520 cm^{-1} [3,43,44] and a small peak at 300 cm^{-1} [47]. Si-II, unstable under lower pressures, is not found in the residual indentation impression. However, in situ Raman spectroscopy performed during nanoindentation found Si-II peaks around 360–370 cm^{-1} [15]. A small, broad peak at 150 cm^{-1} [14,44] and a stronger, wide peak at 470 cm^{-1} [14,44] are associated with a-Si. Si-III and Si-XII exhibit multiple peaks at 166 [47,48], 180–182 [31,36,47], 350–354 [5,14,27,49], 394–400 [14,17,31], 430–436 [1,17,31,44], and 485–488 cm^{-1} [16,48]. The characteristic Si-III/Si-XII spectrum, shown in Fig. 1, reveals a peak at 520 cm^{-1}, contribution from a neighboring Si-I phase, and is not found in materials converted exclusively to Si-III [34]. The Si-III and Si-XII structures are very similar [50], and for simplicity in discussion, these peaks will be presented as a mixture of Si-III/Si-XII [17] in Raman spectra. Finally, a peak at 500 cm^{-1} is observed for Si-IV, but this peak has also been attributed to nanocrystalline Si-I [31] or a shift in the Si-I peak due to residual strain or thermal strain from laser heating. The characteristic peaks used for phase identification are marked with an asterisk (*) in Fig. 1 [17]. Raman spectroscopy is an ideal technique to produce a 2D-phase map of the indent impression, but further confirmation of phases beneath the indent surface is achieved through examination of thin section with TEM.

The purpose of this manuscript is to report the first-ever results of dynamic indentation on silicon and link moderate-strain-rate Si (10^3 s^{-1}) response to quasi-static (strain rate 10^{-2} s^{-1}) and shock pressure testing (strain rate 10^6 s^{-1}). To achieve these goals, single-crystal silicon was subjected to static (15-s duration) and dynamic (100-μs duration) indentations, and the resulting indented regions were scanned with a Raman microscope to assess the phases present. Select areas on static and dynamic indentations were further analyzed with TEM imaging and selected area diffraction (SAD) to complement Raman spectroscopic results.

2. Experimental

An undoped, single-crystal (001) silicon wafer (nominal thickness of 0.5 mm) was utilized in this research. The high quality wafers were obtained from the manufacturer (Kulicke & Soffa Industrial Inc., Fort Washington, PA) in 153-mm-diameter disks. The crystal orientation (001) of the wafer was verified through XRD,