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EFFECT OF LONG-TERM HOLDING UNDER CONTACT LOADING ON THE SPECIFIC FEATURES OF PHASE CHANGES IN SILICON

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It is shown that the long-term holding under the peak load during the indentation of Si (100) leads to the creep of material even at room temperature. This becomes possible due to the phase transition into a more plastic metallic β-Sn phase. The end structural phases in the indentation zone were studied by the micro-Raman spectroscopy. It was discovered that they are affected by the longer holding under the load. Thus, more intense peaks were detected for the amorphous (a-Si) phase in the depth of indentation, as compared with those observed for short-holding indentations. It is suggested that this effect is caused by the activation of the dislocation mechanism in the a-Si formation as a result of the longer action of shear stresses under long-term holding. This fact induces some changes in the kinetics of the events of unloading, which reveal a trend to the formation of "kink pop-out" events instead of the typical "pop-out" and "elbow" events.

Keywords: indentation, silicon, phase transformation, amorphous phase, unloading events, creep, holding time.

Although numerous new materials for micro- and optoelectronics were created within the last years, silicon remains the principal component of the major part of semiconductor devices and has numerous industrial applications. Parallel with electrical and optical properties, the mechanical behavior of Si, especially under local loading, is of especial interest in view of the specific features of its structural phase transformation in nano- or micro-volumes of the deformed material. High pressures created by nano/microindentation lead to the phase transformation of the initial diamond cubic structure (Si-I) into a highly conductive β-Sn structure (Si-II) under loading. If the pressure is released, then Si-II transforms into the body centered cubic (Si-III), rhombohedral (Si-XII) and amorphous (a-Si) structures depending on the rate of unloading [1, 2], value of the load, and the type of indenter [3–5] (or on the deformation temperature [6, 7]).

Recently silicon has found wide applications in microelectromechanical systems (MEMS) whose reliability strongly depends on the mechanical durability of the used material. In the course of exploitation, the Si MEMS components may undergo the influence of long-lasting constant loads. The nanoindentation technique proves to be the most suitable procedure for the investigation of the time-dependent mechanical response of the material under these conditions and to study various aspects of the process of creep on nano- and microscales.

It seems likely that, despite numerous works dealing with the mechanical behavior of Si under nano/microindentation for various loading conditions, such as cyclic loading [3, 8] or scratching [5], there is a gap in the investigations of indentation creep for Si. Thus, the data concerning the characterization of creep in silicon were mostly obtained by using uniaxial compression or bending tests for relatively low stresses (from 2 to 150 MPa) and elevated temperatures (from 800 to 1300°C) [9, 10]. The main deformation mechanism during

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creep was shown to be the dislocation movement, which is obvious for the analyzed range of stresses. Under indentation, however, the conditions of deformation are different: much higher stresses, highly localized strains in nano/micro-volumes resulting in the use of the phase-transformation mechanism of deformation, parallel with the dislocation mechanism. Therefore, the aim of the present work is to investigate the behavior of Si under the indicated conditions and to study the influence of long-term holding under the load on the phase-transformation and deformation features of the material.

Experimental Details

The depth-sensing nanoindentation technique with Berkovich diamond pyramidal indenter was used to induce local deformation in an *n*-type phosphorus-doped Si (100) wafer with a resistivity of $4.5\ \Omega\cdot\mathrm{cm}$. The range of loads included 50, 100 and 500 mN to study the influence of the load value. For each of these loads, we applied two loading modes, including the standard short holding time (5 sec) under the maximum load ($P_{\max}$) and a long holding time (900 sec) under $P_{\max}$. The loading and unloading times were kept equal to 50 sec for all applied loads and holding-time modes. Note that ten indentation tests were performed for each individual combination of load and loading mode. The load versus penetration depth $P(h)$ and penetration depth versus time $h(t)$ dependences were plotted for each realized indentation.

For indentations with longer holding times, the thermal drift estimation was made. To do this, during unloading, at 10% of $P_{\max}$, a 30 sec holding was applied to measure the displacement of the indenter, and the respective corrections to the $P(h)$ curves, including the creep plateau, were done. The mean value of the thermal drift rate was found to be 0.15 nm/sec.

The characterization of phase transformations in the indentation zone was carried out by the micro-Raman spectroscopy with the help of a Monovista confocal Raman spectrometer with a wavelength of 532 nm and a laser focused to a spot of about 2 μm in radius. This type of laser is capable of detection at about 0.8 μm into the depth of the material when focusing on the surface. If we focus the laser at a certain depth, then it becomes possible to study deeper regions of the material below the imprint.

Results and Discussions

Specific Features of the $P(h)$ Dependences. In Fig. 1, we show the typical load-penetration $P-h$ curves for 50 mN, 100 mN, and 500 mN indentations made for short (5 sec) and long (900 sec) holding times. A creep plateau can be seen in the $P-h$ curves for indentations with long holding time, which is not typical of the indentations of hard materials at room temperature. However, in the case of Si, this can be possible due to the phase transformation under loading of the original diamond cubic structure (Si-I) into the β-Sn structure (Si-II), which is a metallic more plastic phase. Thus, it is expected that this phase can be easier extruded under the indenter toward the surface, thus allowing the subsequent penetration of the indenter. This is consistent with the results obtained by Rabier, et al. [11] who demonstrated an exceptional ductility of the β-Sn metallic phase at room temperature in silicon subjected to deformation under a pressure of 15 GPa.

The $P-h$ curves for short-term holding are characterized by the formation of typical “pop-out” and “elbow + pop-out” events under loads of 50 and 100 mN (Figs. 1a, b; curves 1). As the holding time increases, we observed a trend to the formation of a so-called “kink pop-out” (Figs. 1a, b) more often displayed for 100 mN indentations (eight cases out of ten) and more rarely for 50 mN indentations (two cases out of ten); in the remaining cases, the “pop-out” effect is preserved. The 500 mN indentations exhibit the “kink pop-out” events for both short and long periods of holding (Fig. 1c).

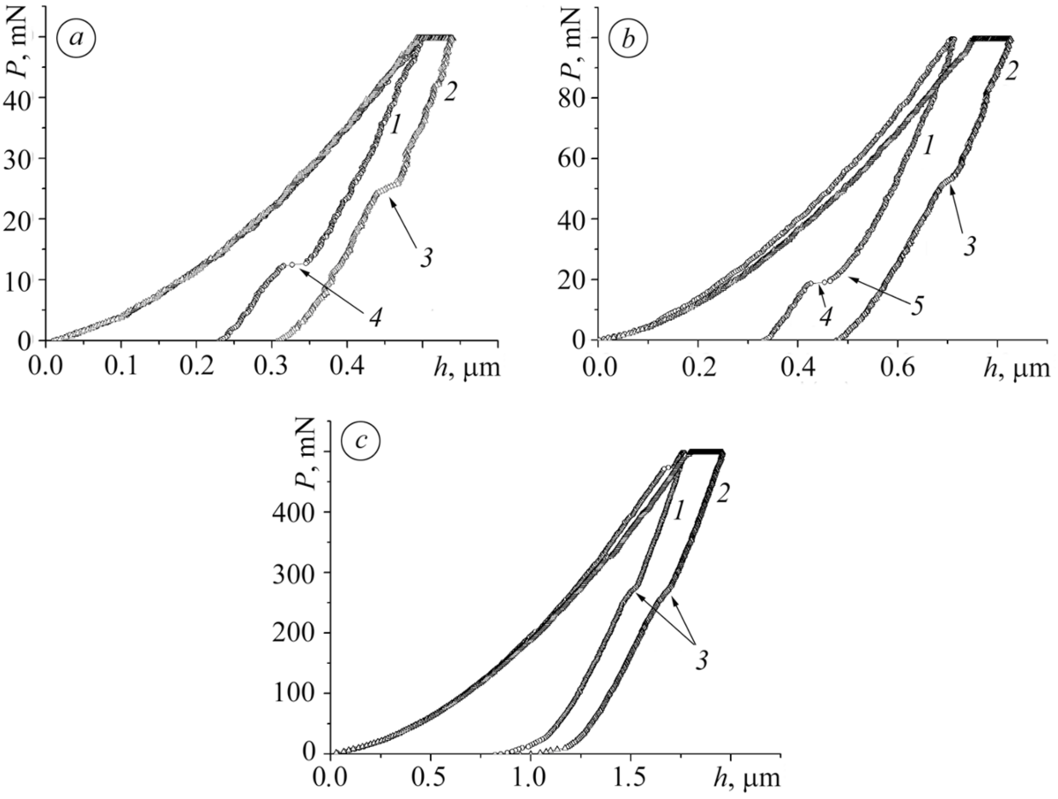

Fig. 1. Load–penetration (*P–h*) curves for indentations made at 50 mN (a), 100 mN (b) and 500 mN (c): (1) short-term holding (50 sec); (2) long-term holding (900 sec). The unloading events: (3) kink pop-out; (4) pop-out; (5) elbow.

The typical unloading events, i.e., "pop-out" and "elbow" were well investigated and discussed in the literature [1, 12]. It was found that they appear as a result of the formation of Si-III/Si-XII and a-Si phases, respectively. It was shown that the "kink pop-out" event relates to the formation of Si-III/Si-XII and, in some cases, to a mixture of Si-III/Si-XII and a-Si, and it appears more frequently under higher loads for lower unloading rates [13].

The causes leading to the appearance of "kink pop-out" events as the holding time increases are not quite clear and should be clarified. The magnified portions of $P-h$ curves containing the unloading events (Fig. 2) display the similarity of "kink pop-out" events with "elbow" events, which are known to be responsible for the a-Si phase formation: Both of these reveal a more gradual pushing out of the indenter caused by the growth of the material volume, as compared with the "pop-out" event, which represents a sharp (hopping) expulsion of the indenter from the material. The evaluation of the derivatives dh/dP of the $P(h)$ dependences for different unloading events is presented in Table 1. The physical meaning of the derivative dh/dP is the rate of recovery of depth as the load decreases, which is nothing but $\cot\alpha$, where α is the slope of the $P-h$ curve (see Fig. 2b). The data presented in Table 1 reveals close values obtained for the "kink pop-out" and "elbow" events, which means that the kinetics of these two processes is also similar.

Micro-Raman Spectroscopy of the Indentations. The micro-Raman spectroscopy of the indentations was carried out in order to find out whether the end structural phases in the indentation zone are affected by long-term holding.

The micro-Raman spectra of indentations taken for both short and long holding times were acquired from the zones located in the immediate proximity to the surface of indentation (Fig. 3; spectra 1, 3) and from the re-

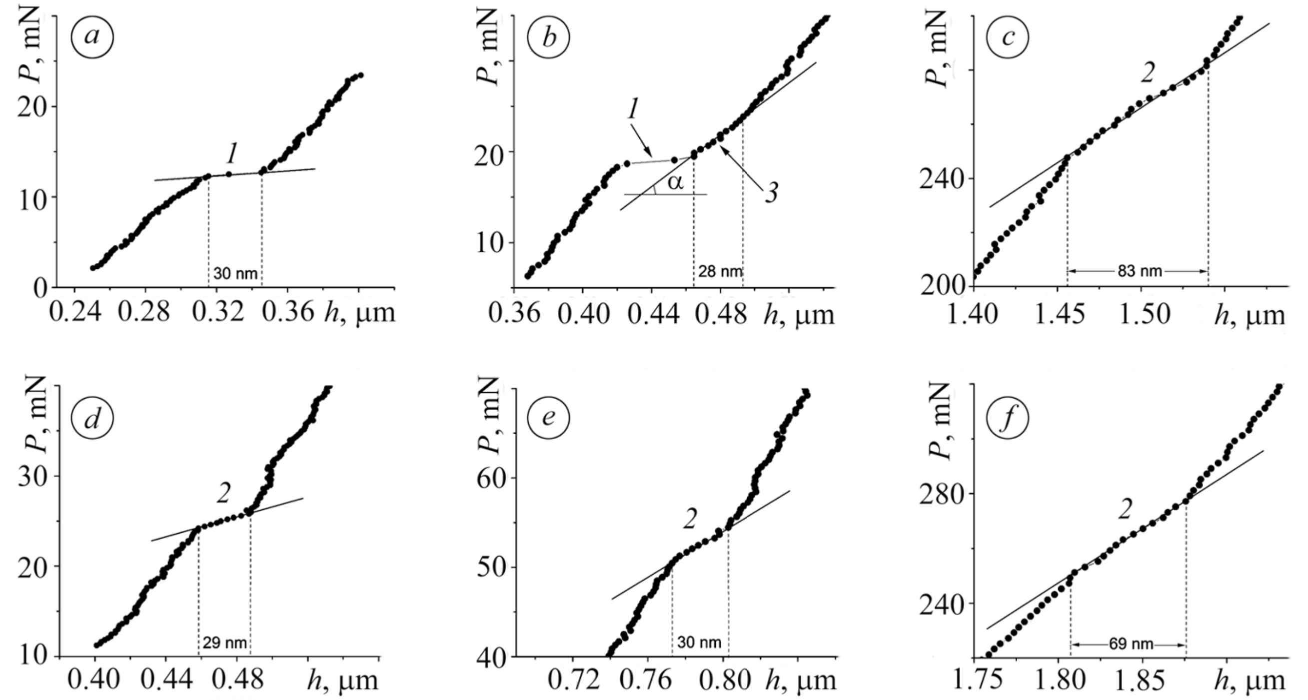

Fig. 2. Magnified fragments of the curves from Fig. 1 containing the unloading events for indentations made with short-term holding (a–c) and long-term holding (d–f) for $P_{\max}$ equal to 50 mN (a, d), 100 mN (b, e), and 500 mN (c, f): (1) pop-out; (2) kink pop-out; (3) elbow.

Table 1. **Derivatives dh/dP for the Events of Unloading in the $P-h$ Curves**

Load, mN	Holding time, sec	Mean values of dh/dP for the unloading event, nm/mN		
		“pop-out”	“elbow”	“kink pop-out”
50	5	77.7	12.8	–
	900	80.2	–	18.1
100	5	76.5	7.0	–
	900	78.7	–	7.5
500	5	–	–	2.4
	900	–	–	2.5

gions located at a certain depth (Fig. 3; spectra 2, 4). It is easy to see that for short-term holding indentations (Fig. 3; spectra 1, 2), the peak responsible for a-Si (470 cm^{-1}) is more pronounced on the surface than in depth.

However, as the holding time increases (Fig. 3; spectra 3, 4), the a-Si peak, on the contrary, becomes more intense in depth [as compared with the Si-XII (350 cm^{-1}), Si-III (372 and 433 cm^{-1}), and Si-I (301 and 520 cm^{-1}) peaks].

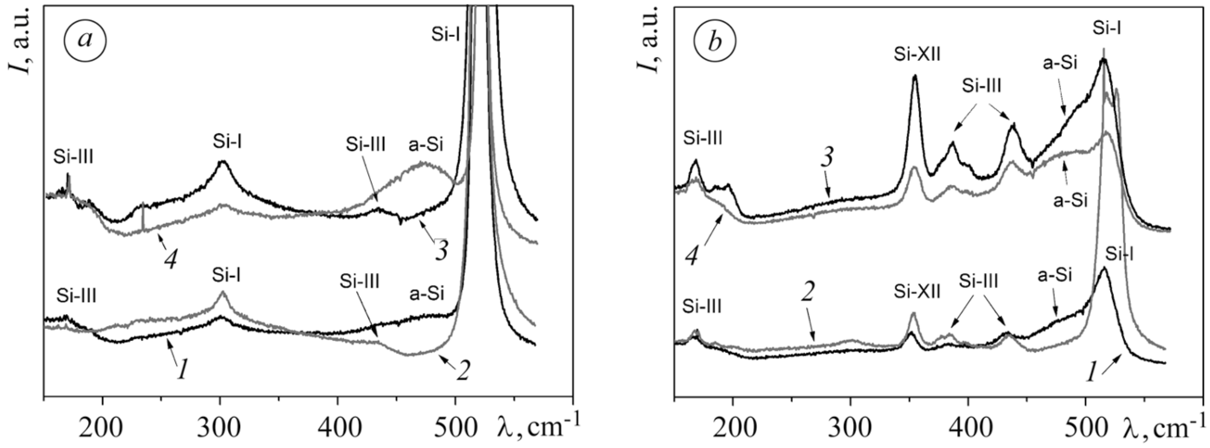

Fig. 3. Micro-Raman spectra for 50 mN (a) and 500 mN (b) indentations obtained from the surface (spectra 1 and 3) and at a certain depth (spectra 2 and 4); spectra 1 and 2 correspond to short-term holding indentations and spectra 3 and 4 correspond to long-term holding indentations.

It was shown by Tachi, et al. [14] that the amorphous phase can be created not only in the immediate vicinity of the indentation surface, where the compressive stresses are maximum, but also in the dislocation zone as a result of the motion of dislocations under plastic deformation in the form of thin layers oriented along the main slip planes {111} of Si. The longer action of the external load may contribute to the intensification of these processes leading to the extension of the amorphous zones. The "kink pop-out" effect on the $P-h$ curves is supposed to be caused by the formation of the amorphous phase as a result of the dislocation activity. As shown above, the kinetics of "kink pop-out" is similar to the kinetics of "elbow," which is known to be the result of formation of the amorphous phase during unloading and this fact is in good agreement with the obtained results of micro-Raman spectroscopy.

The fact that the "kink pop-out" event is more rarely displayed for 50 mN indentations than for 100 mN indentations can be explained by a smaller dislocation region in which the development of the conditions required for the formation of the amorphous phase is less probable.

For 500 mN indentations, the increase in holding time also leads to the intensification of the Si-III and Si-XII peaks as compared with the initial Si-I peak, especially on the surface. This agrees with our previous work on the long-term holding during Vickers quasistatic indentation showing the same results [15]. The broadening of the Si-I peak at $301\,\mathrm{cm}^{-1}$ observed for 50 mN indentations may be caused by the increasing degree of structural disorder due to the high density of dislocations.

Displacement-Time Dependences During Creep. The analysis of the displacement–time dependences plotted during holding under the peak load $(P_{\max})$ reveals some specific features of the creep process. The "penetration-depth–time" curves and the time dependences of the corresponding instantaneous creep rate (the derivative dh/dt) plotted for 50 and 500 mN indentations are shown in Figs. 4a, b and c, d, respectively. It is well visible from the presented curves that the creep process has two different stages: the first stage is distinguished by a higher and, at the same time, decreasing creep rate, whereas in the second (steady-state) creep stage, the creep rate becomes almost constant with a slight decreasing trend.

The initial creep rate appears to depend on the applied load and it is higher (~ 4 nm/sec) for higher peak-load (500 mN) indentations against ~ 1 nm/sec for 100 and 50 mN indentations. In addition, the span of the first stage is also larger for higher loads and equal to about 175, 125, and 100 sec for 500, 100, and 50 mN indentations, respectively. These two specific features explain the larger creep displacements within the same holding

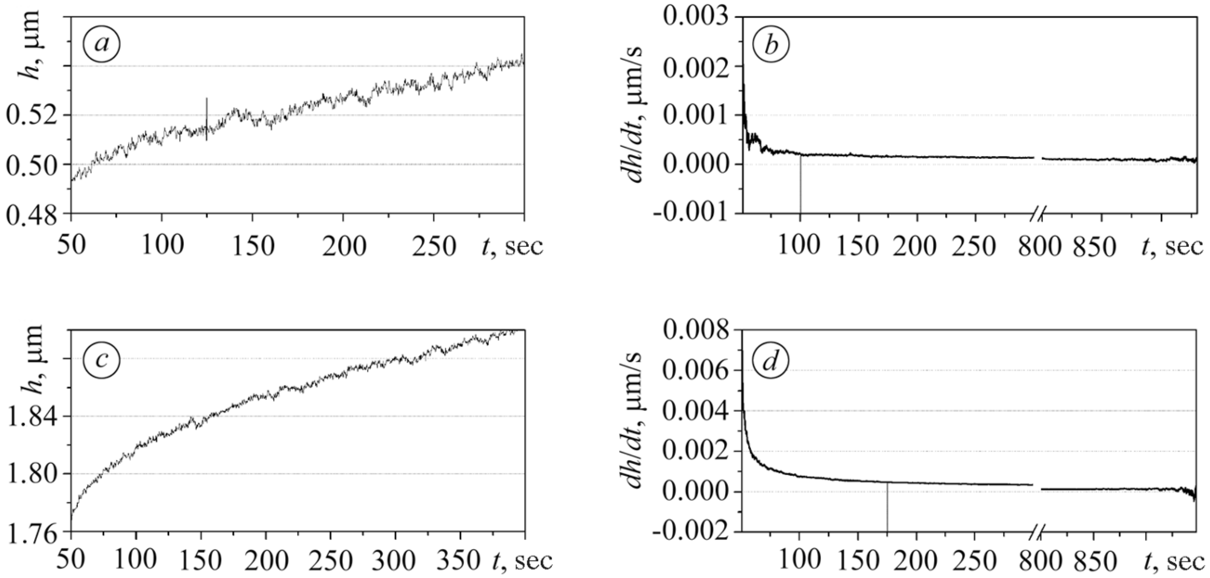

Fig. 4. Displacement-time dependences (a, c) and the "creep-rate–time" dependences (b, d) in the process of creep for 50 mN (a, b) and 500 mN (c, d).

time for higher loads displayed in the $P(h)$ curves (Fig. 1). At the end of the holding period, the creep rate approaches zero.

CONCLUSIONS

The long-term holding under the peak load during indentation was found to affect the deformation behavior of Si (100) manifested by the creep of material, a trend to the formation of "kink pop-out" unloading events instead of the typical "pop-out" and "elbow + pop-out" events, and the changes in phase transformations.

The end structural phases in the indentation zone displayed by the micro-Raman spectroscopy indicate the intensification of formation of the amorphous phase with the increase in the holding time. The cause of this additional amorphization is assumed to have a dislocation nature, as a result of growth of the dislocation density during creep and restructuring of the dislocation zone during unloading. It was suggested that the "kink pop-out" effect is caused by the formation of the amorphous phase in the depth of indentation in the dislocation zone, which is confirmed by the micro-Raman spectra revealing a higher intensity of the a-Si peaks in the deeper regions than in the regions closer to the surface of the indentation. The kinetics of the "kink pop-out" effect displayed by the derivative dh/dP of the $P-h$ curve demonstrates its similarity to the "elbow" effect, which is known to be the result of a-Si formation.

The displacement-time dependences during creep were found to be affected by the value of the load, thus showing higher initial creep rates and then establishing a steady-state creep stage for the indentations made with higher loads, which explains larger creep displacements for these indentations, as compared with the indentations made with lower loads for the same holding time.

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