# EFFECT OF PROLONGED HOLDING UNDER CONTACT LOADING ON THE PECULIARITIES OF PHASE CHANGES IN SILICON

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It was shown that prolonged holding under the peak load during indentation of Si (100) led to the creep of material even at room temperature that became possible due to the phase transition into more plastic metallic β-Sn phase. The end structural phases in the indentation zone, studied by micro-Raman spectroscopy were found to be affected by the longer holding under the load and demonstrated more intensive peaks for amorphous phase (a-Si) in the depth of the indentation comparatively with those for short holding indentations. It was suggested that this effect was caused by the activation of the dislocation mechanism of a-Si formation, as a result of longer shear stresses action under prolonged holding. This fact induced some changes in the kinetics of the unloading events, which demonstrated the tendency to the "kink pop-out" formation instead of typical "pop-out" and "elbow".

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

Although a lot of new materials for micro- and optoelectronics have been elaborated within the last years, silicon remains the principal component of most semiconductor devices and has many industrial uses. Along with electrical and optical properties, mechanical behaviour of Si, especially under local loading, obtained a special interest due to its peculiarity for structural phase transformation in nano- or micro-volumes of deformed material. High pressure created under nano/microindentation leads to the phase transformation of initial diamond cubic structure (Si-I) into high conductive β-Sn structure (Si-II) under loading. On pressure release Si-II transforms into body centered cubic (Si-III), rhombohedral (Si-XII) and amorphous (a-Si) structures depending on the unloading rate [1, 2], load value, type of indenter [3–5] or deformation temperature [6, 7].

Recently silicon has found a wide application in micro-electro-mechanical systems (MEMS), the reliability of which strongly depends on the mechanical durability of material used. During exploitation the Si MEMS components can undergo the influence of long lasting constant load. The nanoindentation technique is the most suitable one to investigate the time-dependent mechanical response of material in such conditions and to study various aspects of creep process at nano- and microscale.

In spite of a lot of works concerning the mechanical behaviour of Si under nano/microindentation at various loading conditions like cyclic loading [3, 8] or scratching [5], apparently there is a gap in indentation creep investigations on Si. Mostly the data regarding the silicon creep characterization were obtained using uniaxial compression or bending tests for comparatively low stresses (from 2 to 150 MPa) and enhanced temperatures (from 800 to 1300°C) [9, 10]. The main deformation mechanism during creep was shown to be the dislocation movement that is obvious for the used range of

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stresses. Under indentation, however, the deformation conditions are dissimilar: much higher stresses, highly localized strain in nano/micro-volume, resulting in the involving of the phase transformation mechanism of deformation, besides the dislocation one. Therefore the aim of this work was to investigate the behaviour of Si in these conditions and to study the influence of long lasting holding under the load on the phase transformation and deformation peculiarities of material.

**Experimental details.** The depth-sensing nanoindentation technique with Berkovich diamond pyramidal indenter was used to induce local deformation on n-type, phosphorous-doped Si (100) wafer of a resistivity of 4.5 Ω·cm. The range of loads included 50, 100 and 500 mN to study the influence of load value. For each of these loads we applied 2 loading regimes, including standard short holding time (5 s) under the maximum load ($P_{max}$) and long holding time (900 s) under $P_{max}$. The loading and unloading time was maintained 50 s for all loads and holding time regimes used. For each separate combination of load and loading regime 10 indentation tests were performed. The load versus penetration depth $P(h)$ and penetration depth versus time $h(t)$ dependences were acquired for each indentation made.

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

The phase transformation characterization of the indentation zone was carried out by micro-Raman spectroscopy using Monovista confocal Raman spectrometer with 532 nm wavelength laser focused to a spot of about 2 μm radius. This type of laser is able to detect about 0.8 μm into the depth of the material when focusing at the surface. By using the focusing of the laser in some depth it became possible to investigate deeper regions of the material underneath the imprint.

**Results and discussions.** ***Peculiarities of P(h) dependences.*** Fig. 1 shows the typical load-penetration *P–h* curves for 50 mN, 100 mN and 500 mN indentations made at short (5 s) and long (900 s) holding time. A creep plateau can be seen on the *P–h* curves for long holding time indentations, which is not typical for room temperature

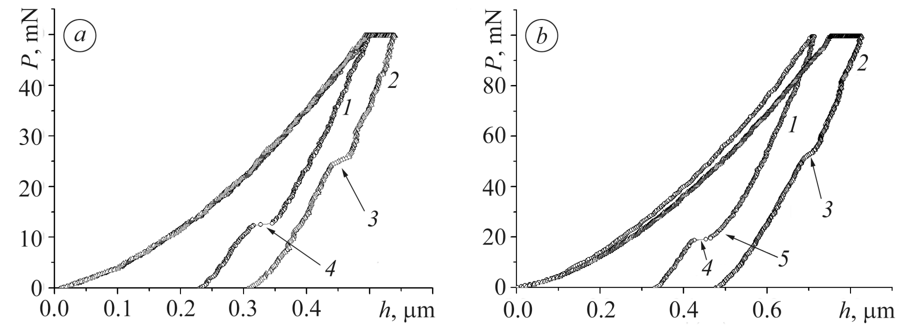
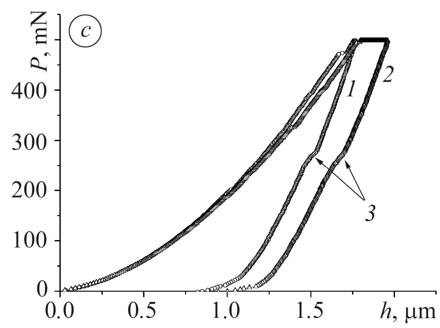



Fig. 1. Load–penetration (*P–h*) curves of indentations made at 50 mN (*a*), 100 mN (*b*) and 500 mN (*c*):
*1* – short holding (50 s);
*2* – long holding (900 s).
The unloading events:
*3* – kink pop-out;
*4* – pop-out; *5* – elbow.



indentation of hard materials. But in the case of Si this can be possible due to the phase transformation during loading of the initial diamond cubic structure (Si-I) into the β-Sn structure (Si-II), which being a metallic, more plastic phase is expected to be extruded more easily underneath the indenter toward the surface allowing further penetration of the indenter. This is consistent with the results obtained by Rabier et al. [11] demonstrating an exceptional ductility of β-Sn metallic phase at room temperature during silicon deformation under a pressure of 15 GPa.

The *P*–*h* curves for short holding are characterized by the formation of typical "pop-out" and "elbow + pop-out" events in the case of 50 and 100 mN load applied (Fig. 1*a*, *b*, curves *1*). With the increase of holding time the tendency to the formation of a so-called "kink pop-out" was observed (Fig. 1*a, b*), more often displayed for 100 mN indentations (8 cases from 10) and more rarely for 50 mN indentations (2 cases from 10); in the rest of the cases the "pop-out" effect is maintained. The 500 mN indentations exhibit the "kink pop-out" for both short and long holding time (Fig. 1*c*).

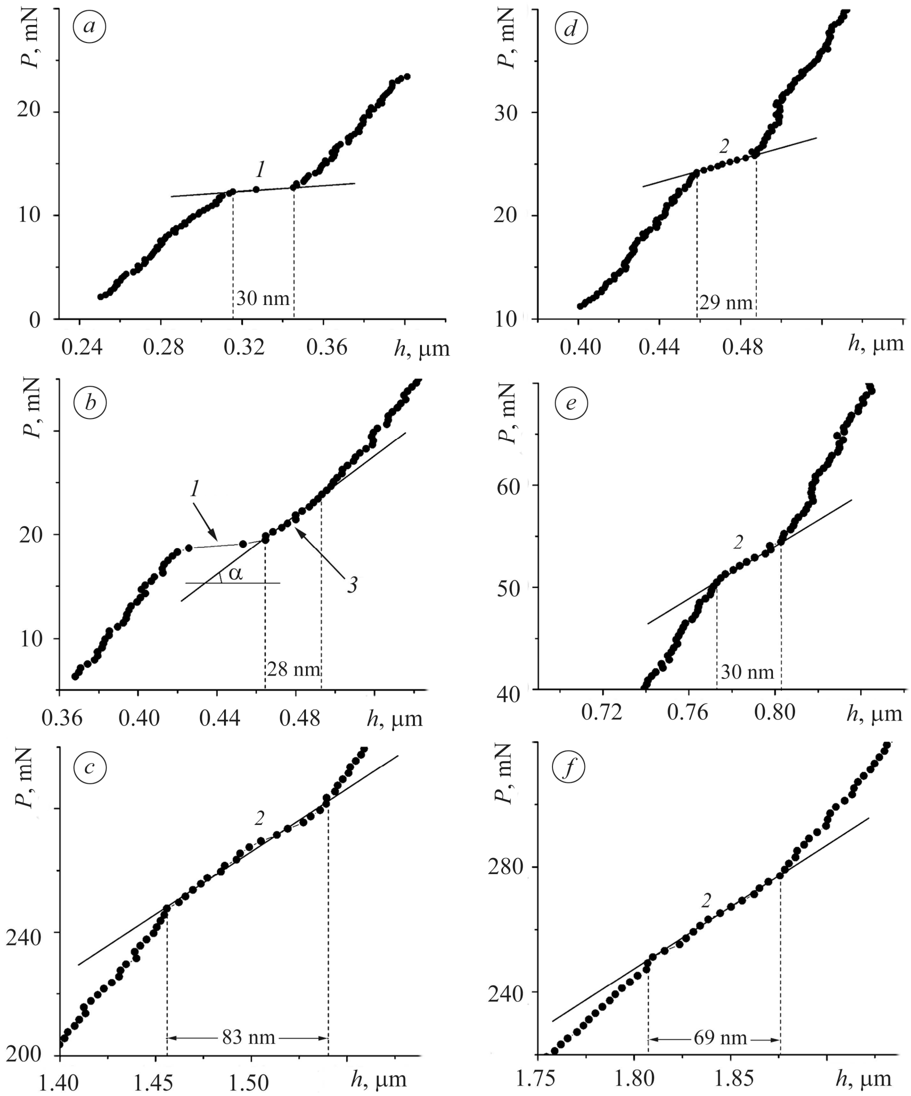



Fig. 2. Magnified fragments of curves from Fig. 1 containing the unloading events of indentations made under short holding (*a*–*c*) and long holding (*d*–*f*) at $P_{max}$ equal to 50 mN (*a*, *d*), 100 mN (*b*, *e*) and 500 mN (*c*, *f*): *1* – pop-out; *2* – kink pop-out; *3* – elbow.

The typical unloading events – "pop-out" and "elbow" were well investigated and discussed in the literature [1, 12] and were found to be the result of the formation of Si-III/Si-XII and a-Si phases respectively. The "kink pop-out" was shown to be related to the formation of Si-III/Si-XII and in some cases to a mixture of Si-III/Si-XII and a-Si and appeared more frequently for higher loads and slower unloading rates [13].

The reasons leading to the "kink pop-out" emergence with the increase of holding time are not quite clear and have to be clarified. The magnified portions of $P$–$h$ curves containing the unloading events (Fig. 2) display the similarity of "kink pop-out" event with "elbow" one, which is known to be responsible for the a-Si phase formation: both of them demonstrate more gradual pushing out of the indenter caused by the growth of material volume, comparatively with the "pop-out", which represents a sharp, hopping expulsion of the indenter from the material. The calculations of the derivatives $dh/dP$ of the $P(h)$ dependences for different unloading events are presented in Table. The physical meaning of $dh/dP$ represents the rate of the depth recovery at load decrease, which is none other than ctg$\alpha$, where $\alpha$ is the slope of the $P$–$h$ curve (see Fig. 2*b*). The data from Table showed close values between "kink pop-out" and "elbow" events indicating that the kinetics of these two processes is similar as well.

**Derivatives *dh*/*dP* for the unloading events on the *P*–*h* curves**

| Load, mN | Holding time, s | 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 |

***Micro-Raman spectroscopy of indentations.*** The micro-Raman spectroscopy of indentations were carried out in order to find out whether the end structural phases in the indentation zone are affected by prolonged holding.

The micro-Raman spectra of indentations made at both short and long holding time were acquired from the zones situated in immediate proximity to the surface of indentation (Fig. 3, spectra 1, 3) and from the regions situated at some depth (Fig. 3, spectra 2, 4). One can see that for short holding indentations (Fig. 3, spectra 1, 2) the peak responsible for a-Si (470 $cm^{-1}$) is more pronounced at the surface than in the depth, but with the increase of holding time (Fig. 3, spectra 3, 4) just vice-versa, the a-Si peak becomes more intensive in the depth (to compare with Si-XII (350 $cm^{-1}$), Si-III (372 and 433 $cm^{-1}$) and Si-I (301 and 520 $cm^{-1}$) peaks).

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

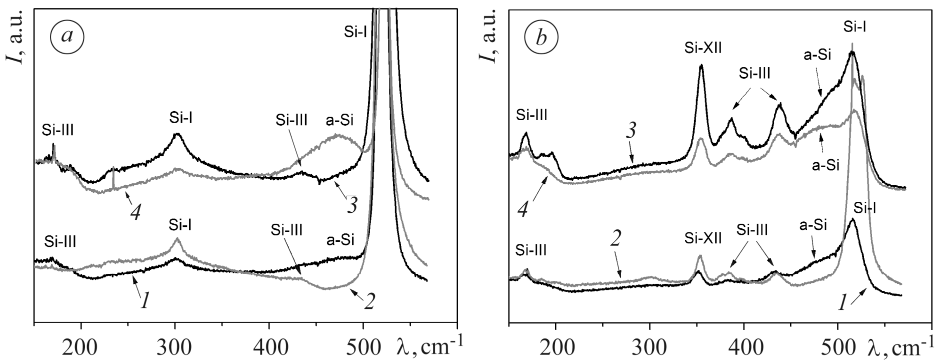



Fig. 3. Micro-Raman spectra of 50 mN (*a*) and 500 mN indentation (*b*), acquired from the surface (spectra 1, 3) and from some depth (spectra 2, 4); spectra 1, 2 – short holding, and spectra 3, 4 – long holding indentations.

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

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

***Displacement-time dependences during creep.*** The analysis of displacement-time dependences during holding at the peak load ($P_{max}$) displayed some peculiarities of creep process. The penetration depth versus time curves and the respective instantaneous creep rate (derivative $dh/dt$) versus time curves for 50 and 500 mN indentations are shown accordingly in Fig. 4 (*a*, *b*) and (*c*, *d*). It is clearly seen from the curves presented that the creep process has 2 distinctive stages: the first one distinguished by higher and at the same time decelerating creep rate and the second, steady-state creep stage, where the creep rate becomes almost constant with a slight decreasing tendency.

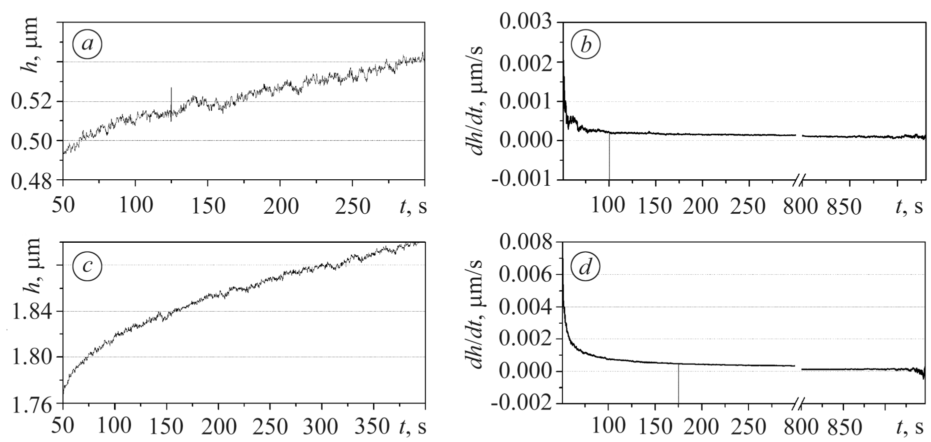



Fig. 4. Displacement-time dependences (*a*, *c*) and creep rate versus time dependences (*b*, *d*) during creep for 50 mN (*a*, *b*) and 500 mN (*c*, *d*).

The initial creep rate appears to depend on the load applied and it is higher (~ 4 nm/s) for larger peak load (500 mN) indentations against ~ 1 nm/s for 100 and 50 mN indentations. In addition, the span of the first stage is also larger for larger load and it is about 175, 125 and 100 s for 500, 100 and 50 mN indentations, respectively. These two peculiarities explain the larger creep displacement within the same holding time for higher loads displayed on $P(h)$ curves (Fig. 1). To the end of holding period the creep rate approaches to zero.

**CONCLUSIONS**

The prolonged holding under the peak load during indentation was found to influence the deformation behaviour of Si (100) manifested by creep of material, tendency to the formation of “kink pop-out” unloading event instead of typical “pop-out” and “elbow + pop-out” events as well as changes in phase transformation.

The end structural phases in the indentation zone displayed by micro-Raman spectroscopy indicate the intensification of the amorphous phase formation with the increase of holding time. The reason of this additional amorphization was assumed to have a dislocation nature, as a result of growth of dislocation density during creep and restructuring of 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 that is confirmed by the micro-Raman spectra demonstrating higher intensity of 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.

Displacement-time dependences during creep were found to be influenced by the load value showing higher initial creep rate and tardier establishing of a steady-state creep stage for the indentations made with higher load that explains the larger creep displacement for them comparatively with indentations made with lower load at the same holding time.

*РЕЗЮМЕ*. Досліджено вплив тривалої витримки під час індентування на особливості фазових перетворень і деформації кремнію Si (100). Показано, що тривала витримка за максимального навантаження призводить до повзучості матеріалу навіть за кімнатної температури завдяки фазовому перетворенню на пластичнішу металеву $\beta$-Sn фазу. Кінцеві структурні фази в зоні відбитка, виявлені за допомогою мікро-Рамановської спектроскопії, вказують на інтенсифікацію утворення аморфної фази (a-Si) зі зростанням часу витримки. Передбачається, що причина цієї додаткової аморфізації може мати дислокаційну природу, як результат зростання щільності дислокацій під час повзучості і перебудови дислокаційної структури під час розвантаження. Цей факт вносить деякі зміни до кінетики розвантажувальних явищ, які демонструють тенденцію до утворення “kink pop-out” замість типових “pop-out” і “elbow”.

*РЕЗЮМЕ*. Исследованно влияние длительной выдержки при индентировании на особенности фазовых превращений и деформирования кремния Si (100). Показано, что длительная выдержка при максимальной нагрузке ведет к ползучести материала даже при комнатной температуре благодаря фазовому превращению в более пластическую металлическую $\beta$-Sn фазу. Конечные структурные фазы в зоне отпечатка, выявленные посредством микро-Рамановской спектроскопии, указывают на интенсификацию образования аморфной фазы (a-Si) с ростом времени выдержки. Предполагается, что причина этой дополнительной аморфизации может иметь дислокационную природу, как результат роста плотности дислокаций во время ползучести и перестройки дислокационной структуры во время разгрузки. Этот факт вносит некоторые изменения в кинетику разгрузочных явлений, которые демонстрируют тенденцию к образованию “kink pop-out” вместо типичных “pop-out” и “elbow”.

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