Influence of Loading Holding Time under Quasistatic Indentation on Electrical Properties and Phase Transformations of Silicon

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The quasistatic Vickers indentation of Si (100) were applied to investigate the influence of loading holding time on the changes of electrical resistance and phase transformation in the indentation zone. For all used loading regimes with different holding times (2 s, 10 s, 1 h and 10 h) in combination with constant loading-unloading rate (250 mN/s) the electrical resistance in the region of residual indentations was found to be lower than before indentation. It was shown that this is connected with the formation of semimetallic Si-III phase and amorphous Si of higher pressure induced by creep process developed under long lasting pressure. The longer the holding time, the greater lowering of electrical resistance in the indentation region was observed, with the exception of the holding time above 1h, this being explained by a decelerating creep rate of Si for this interval of time leading to a halt of further extending of amorphous and Si-III regions of lower electrical resistance.

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INTRODUCTION

Being one of the most used materials for microelectronics, optoelectronics, micro- and nano-electromechanical systems, silicon is widely investigated from the point of view of its mechanical behavior for the purpose of deeper understanding of processes taking place under mechanical impact during fabrication and exploitation of devices on its base, as well as with the view of the possibility of using its mechanical peculiarities for the creation of special functional structures and surfaces. Recently, considerable attention has been paid to the structural modification of the silicon single crystal under the influence of the concentrated load action (nanoindentation and microindentation). It is known that Si undergoes a series of phase transformations under high local stresses created during micro- and nanoindentation: the initial diamond cubic phase (Si-I) transforms into β-Sn phase (Si-II) during loading at the contact pressure of about 8–12 GPa, and during unloading, under the pressure release, R8 (Si-XII) and BC8 (Si-III) phases at 5–8 GPa and amorphous (a-Si) phases at about 4 GPa were found to be formed [1–3].

So far under investigation were the influence of different factors and loading conditions such as temperature of deformation [4–6], unloading rate [7, 8], load value and type of indenter [2, 3], cyclic loading-unloading [3, 9, 10] on the peculiarities of phase transformations. Theoretical predictions of silicon behavior under high pressure and experimental investigations under hydrostatic pressure in a diamond anvil cell demonstrated that Si-II is a highly conductive metallic phase [11], Si-XII and Si-III are semimetals [12, 13], and amorphous Si is a narrow-bandgap semiconductor at ambient pressure, exhibiting metallic properties under enhanced pressure [14]. Therefore along with Raman spectroscopy [1, 3–8] and transmission electron microscopy investigations [2, 3, 9], for studying indentation-induced phase transformations in Si, the in-situ measurements of electrical resistance changing in the indentation zone are successfully applied [3, 4, 9, 15] and demonstrate a good correlation with the structural phase formation sequence during the loading-unloading cycle.

Another factor, besides the mentioned above, modeling an eventual condition that could be created during manufacturing and functioning of Si based devices, is the prolonged holding under the local loading that could induce some specific changes in structural transformation of Si. This factor can be investigated by increasing the holding time under the peak load during indentation, which is known to cause the creep (continued deformation under the constant load) for some materials. However the present work does not involve the investigation of the indentation creep directly, although it is an apart interesting problem. The aim of this work is the investigation of electrical resistance and phase transformation changing induced by long lasting constant loading, these changes being obviously influenced by the process of creep deformation and relaxation of material.

EXPERIMENTAL DETAILS

The quasistatic microindentation technique with the Vickers diamond tetrahedral pyramidal indenter was used to induce local deformation on an n-type, phosphorous-doped Si (100) wafer of a resistivity of

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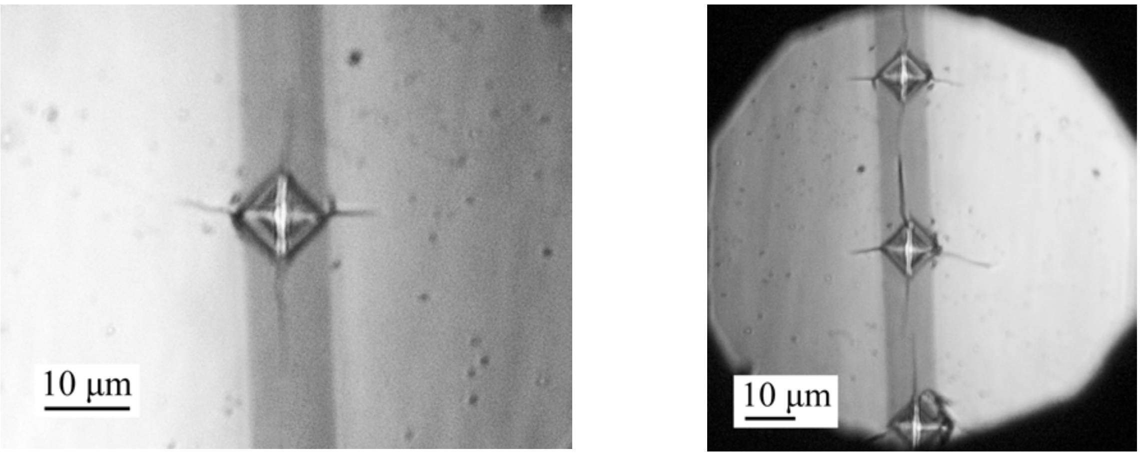
4.5 Ω cm. In order to investigate the influence of the holding time (t_h) under the maximum load several loading regimes were applied: the first one – with standard holding under the load about 3 s, other ones – with longer holding time (10 s, 1 hour and 15 hours). The loading and unloading time cannot be controlled automatically for quasistatic microindentation technique and typically is equal to approximately 2 s, therefore the loading–unloading rate depends on the load value applied to the indenter. In our experiments we used 500 mN load, and the loading–unloading rate was about 250 mN/s, respectively, and remained constant for all loading regimes used. It is important for the investigation of the holding time influence in order to exclude the influence of unloading rate, which is known to affect the formation of one or another phase of Si during pressure release under indentation [7, 8].

For the measurements of electrical resistance of Si in the indentation zone, a special covered structure was prepared: the silicon specimen was covered by Ni leaving a 10 µm strip of uncovered Si. The indentations were made on a Si strip bridging the two Ni covered regions (fig. 1). The current-voltage (I-V)-characteristics of the Si strip were measured before and after indentation on the solar cell tester “ST-1000”. To mark the exact place of electrical probe application (before and after indentation) and to protect the Ni metallic coating, small In contacts were made above the Ni coating from both sides of the Si strip at the equal distance from it. From the obtained V-I dependences, calculations of residual changes of resistance induced by indentation were made.



a *b*

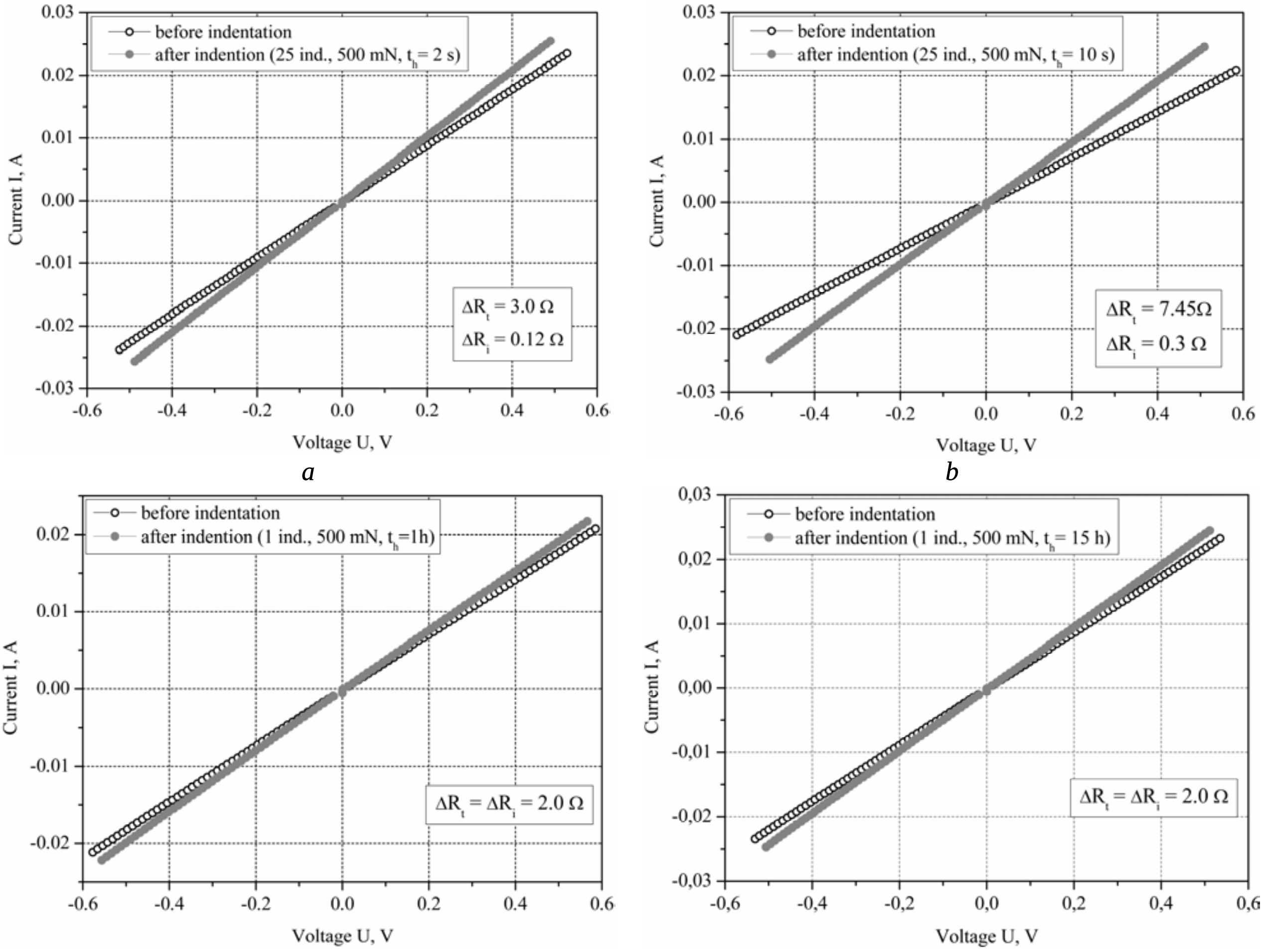
Fig. 1. 500 mN indentations made on Si strip between two Ni covered regions:
a – one indentation on Si strip; b – fragment of a range of 25 indentations on Si strip.

The phase transformation characterization of the indentation zone was performed by micro-Raman spectroscopy using a Monovista confocal Raman spectrometer with a 532 nm wavelength laser focused to a spot with the radius of about 2 µm.

RESULTS AND DISCUSSION

The measurements of the I-V characteristics of the Si strip before and after indentation for all loading regimes are presented in fig. 2. In order to obtain more perceptible result of the I-V characteristics for indentations with the holding time of 2 s and 10 s, 25 bridging indentations were made on the Si strip with a constant pitch (fig. 1,*b*) and the I-V measurements were performed: first, of the Si strip without indentations and then with 25 indentations (fig. 2,*a,b*). For the holding time of 1h and 15 h only one indentation was made on the Si strip (fig. 1,*a*). It should be noted that only one uncovered Si strip was made on each Si specimen, which was used only once to induce deformation by means of indentation and to measure the I-V dependences before and after indentation. The changes of resistance before and after indentation calculated from the I-V dependences (fig. 2) are given in table. One can see that after indentation of the Si strip its resistance decreases for all time-loading regimes used. The value of the drop of resistance (ΔR_i) calculated per one indentation increases with the increase of the holding time under the load. However, this increase of ΔR_i occurs for the holding times up to 1 h, while for longer holding time (15h) no further increase of ΔR_i, was observed, and ΔR_i, remained the same as it was for 1 h holding time.

Although for the case of 25 indentations on the Si strip, the indentations apparently could be considered as parallel connection of conductors, it is not an appropriate scheme for the calculation of the drop of resistance per one indentation (ΔR_i). The structurally transformed regions in the residual indentation, which can induce the drop of resistance, do not always have continuous character, nor strictly bridge the two Ni covered regions, but may represent several discrete zones of irregular shape [16]. In this case, most probably, the transformed semimetallic or metallic zones of indentations enrich the Si strip region as a whole with current carriers, thus lowering its resistance. To find the contribution of each indentation into this process, we divided the total drop of resistance (ΔR_t), calculated from the I-V dependences, by the number of indentations on the Si strip (in our case – 25) and hence obtained the value of ΔR_i.



a *b*

c *d*

Fig. 2. I-V characteristics of Si strip before and after indentation with load P = 500 mN and holding time (t_h): 2 s (a), 10 s (b), 1 h (c), 15 h (d). a, b – 25 indentations and c, d – one indentation on Si strip.

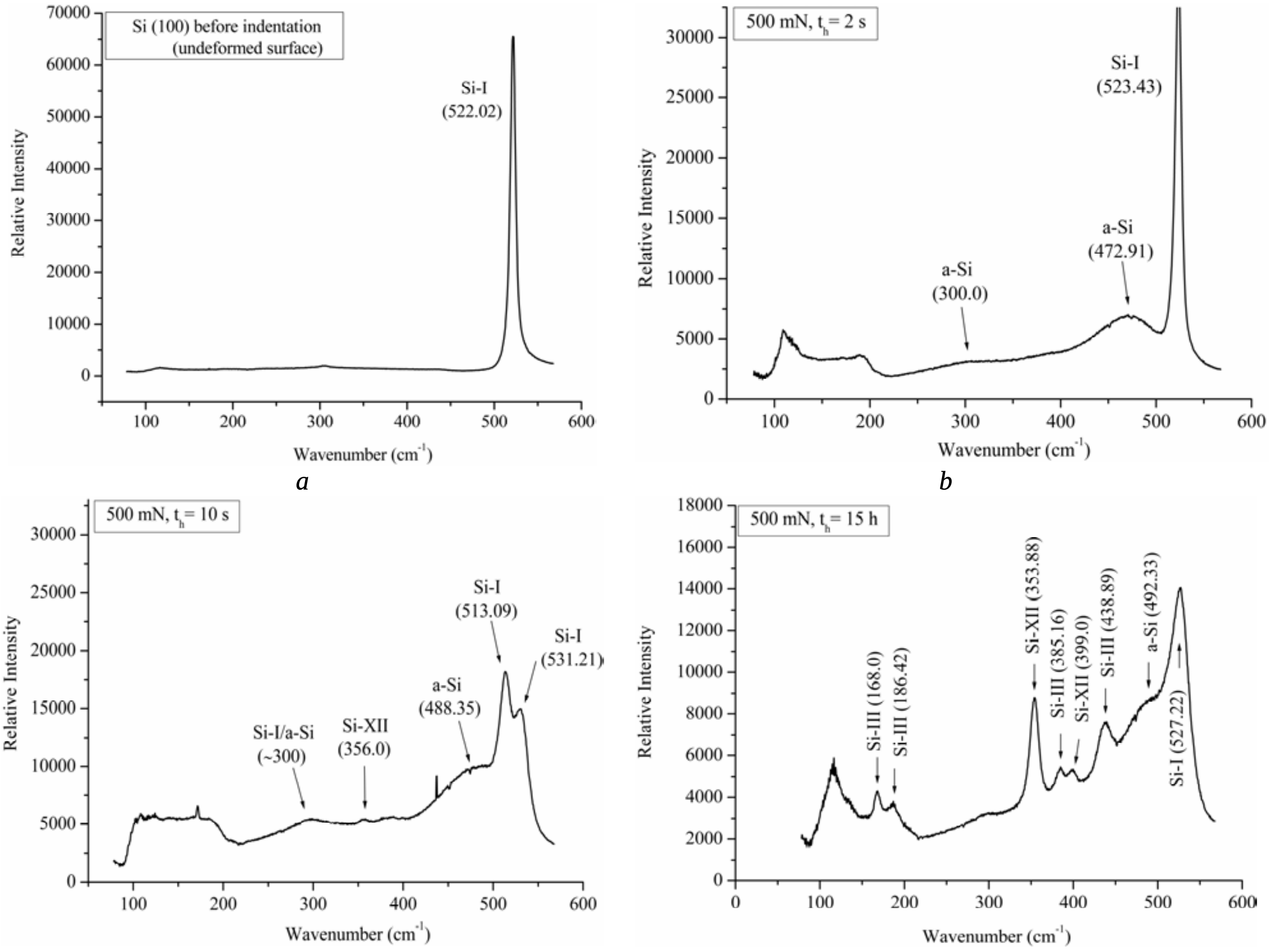
Influence of holding time under load during indentation on changes of electrical resistance of Si in indentation region

Load (P), mN	Loading/ unloading rate, mN/s	Holding time under the max load (t_h), s, hours	Number of indentations	R before indentation, Ω	R after indentation, Ω	Total drop of resistance (ΔR_t), Ω	Drop of resistance per indentation (ΔR_i), Ω /ind.
500	250	2 s	25	22.0	19.0	3.0	0.12
		10 s	25	27.78	20.33	7.45	0.3
		1 h	1	27.3	25.3	2.0	2.0
		15 h	1	22.72	20.73	2.0	2.0

The changing of electrical resistance induced by increasing the holding time during indentation could be the result of some structural phase transformations of Si in the indentation region, which were investigated by micro-Raman spectroscopy. The results of these investigations are shown in fig. 3. For the standard holding time of 2s, Raman spectra demonstrate the presence of an amorphous phase (fig. 3,*b*) that is the result of a high unloading rate [7, 8], which, in turn, leads to the disordering of Si-II lattice and the formation of a-Si. The increase of the holding time up to 10 s contributes to more pronounced evidence of a-Si and a little evidence of Si-III on Raman spectra (fig. 3,*c*). In addition, one can see that the peak responsible for the initial Si-I structure splits into two distinct ones, with Raman scattering frequency of

513.09 and 531.21 cm^{-1}. This is caused by tensile and compressive stresses, which are present in the indentation zone; tensile stresses result in a decrease of Raman frequency, while compressive ones give rise to it [17]. Usually the compressive stresses are concentrated in the centre of the indentation and the tensile stresses are situated at the sides of the indentation, where the material is extruded underneath the indenter.

The indentations made at the holding time of 1 h and 15 h exhibit a well pronounced formation of Si-III and Si-XII phases along with the amorphous one, clearly defined on Raman spectra for 15 h indentation (fig. 3,*d*); 1 h indentation, not shown here, has a similar spectrum. Basing on this result and considering the Si-I into Si-II transformation during indentation under similar conditions [4], it can be assumed that with the increase of the loading holding time the volume of Si-II metallic phase also increases. This metallic more plastic phase is extruded underneath the indenter and gradually depressurized transforming into Si-XII and Si-III structures. This transformation is known to take place during slow unloading [7, 8], but here it appears, most probably, during holding under a constant load. Further, during fast unloading, the amorphous phase is formed as a result of a quick pressure release of the remnant Si-II.



a *b*

c *d*

Fig. 3. Raman spectra of un-deformed Si (100) (a) and of 500 mN indentations in Si (100) made with loading holding time: 2 s (b), 10 s (c) and 15 h (d).

These considerations can explain the observed changes of electrical resistance, induced by indentations with different loading holding time. A lower resistance of Si in the residual indentation neighborhood, we assume, is caused by two reasons. One is the formation of amorphous Si, a part of which remains under pressure even under complete unloading. This can take place especially for the regions of amorphous Si situated at some depth from the indentation surface and surrounded by a high-density dislocation structure. Such regions of amorphous Si in the form of thin slices, the location of which corresponds to the dislocation slip planes, were revealed by TEM investigations [2, 16]. An approximated value of the compressed stress created in the indentation zone can be estimated from Raman spectra knowing that for Si the Raman frequency (wavenumber) changes as small as ~0.02 cm^{-1} correspond to a stress sensitivity of about 10 MPa [17]. The shift of Si-I peak from 522.02 cm^{-1} for undeformed Si (fig. 3,*a*) to 531.21 cm^{-1} or 527.22 cm^{-1} in the indentation region (fig. 3,*c,d*) corresponds to the compressive stresses of 5.6 GPa and 3.71 GPa, respectively. Experimental studies showed that at the pressure of 10 GPa, amorphous

Si transforms into a high-density amorphous phase with metallic properties and, accordingly, this transformation is accompanied by a sharp drop of resistivity. It should be noted, that with the increase of pressure from ambient one to 10 GPa the resistivity also decreases, but gradually [14]. Although for pressures up to ~8 GPa the resistivity of a-Si is higher than that of Si-I [13], for the case of indentation this pressure threshold could be lower due to non pure hydrostatic pressure, involving deviatoric components and high shear stresses, created under indentation. These conditions are known to decrease the transition pressures as compared with pure hydrostatic environment [4, 7, 18]. Relying on the above, it is possible to assume that the compressive stress in the indentation zone can lead to the lowering of the electrical resistance at the expense of amorphous phase under pressure, even if it does not reach the semiconductor-metal transition.

During the holding under the load the volume of the amorphous phase under pressure can increase. It derives from the suggestion that amorphous regions, especially those situated at some depths from the indentation surface, mentioned above, are created as a result of the activation of many dislocations [2]. The increase of the holding time leads to a longer action of shear stresses, which, in turn, contributes to the development and changing of the dislocation structure, thus favoring the formation of the amorphous phase. The increase of the volume of the amorphous phase under pressure of a lower electrical resistance causes the decrease of the electrical resistance in the indentation region with the increase of the holding time, which was revealed by the I-V measurements (table).

Another reason of electrical resistance decrease with the increase of the holding time is connected with the enhanced formation of Si-III and Si-XII phases, especially for the holding time of 1 h and 15 h that is clearly seen on Raman spectra (fig. 3,*d*). Being semimetals of a lower electrical resistance in comparison with Si-I, larger volumes of Si-III and Si-XII lead to the decrease of electrical resistance in the indented region, in particular, for the indentations made with 1h and 15 h holding time (table).

The fact that the increase of the holding time from 1 h to 15 h did not give further increase of ΔR can be explained by the following considerations. As was mentioned above, the holding under the load leads to the creep of material. The investigation of the Si creep under bulk uniaxial deformation showed a specific s-shape dependence of the creep strain on time: accelerating creep rate on the first stage, steady-state creep rate on the second stage and a decelerating creep rate at the final stage [19]. Our investigations on the indentation creep of Si not shown here, demonstrates similar creep behaviour. The formation of the amorphous, Si-III and Si-XII phases during the holding time under the load depends on the development of one or another stage of the creep strain. By increasing the holding time above 1 h the creep process enters its final stage with the decelerating creep rate that means, in fact, a gradual coming to a stop of creep deformation. This leads to a halt of further extending of the amorphous, Si-III and Si-XII regions of a lower electrical resistance, which explains the same values of ΔR for the holding time of 1 h and 15 h.

The I–V measurements of the indented Si strip were repeated after 10 and 30 days for all loading regimes. The results showed the stability in time of the effect of a lower electrical resistance induced by indentation: ΔR remains the same as it was just after indentation, for all holding times used.

CONCLUSIONS

Application of different loading holding times: 2 s, 10 s, 1 h and 15 h, during Vickers indentation demonstrates that after complete unloading, i.e. for residual indentations, the electrical resistance in the indentation region remains lower than before indentation. The longer the holding time, the greater lowering of electrical resistance in the indentation region was observed, with the exception of the holding time above 1h. This is explained by additional structural-phase transformation of Si induced by a long lasting pressure during holding under the load, resulting in the development of the creep process accompanied by the formation of Si-III, Si-XII phases and amorphous Si of higher pressure.

The increase of the holding time above 1h does not give any further lowering of electrical resistance in the indentation zone that can be caused by the entering in the final stage of the creep process characterized by the decelerating creep rate and leading to a halt of further extending of the amorphous, Si-III and Si-XII regions of lower electrical resistance.

The effect of lowering the electrical resistance in the indentation region showed a stable behaviour in time, demonstrating invariable results after 10 and 30 days, for all loading regimes used.

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Реферат

В работе был применен метод квазистатического индентирования по Виккерсу для исследования влияния времени выдержки под нагрузкой на изменение электрического сопротивления и фазовых превращений в зоне индентирования на Si (100). Для всех использованных режимов нагружения с различным временем выдержки под нагрузкой (2 с, 10 с, 1 час и 10 часов) в сочетании с постоянной скоростью нагружения-разгрузки (250 мН/с) было найдено, что электрическое сопротивление в области остаточных отпечатков имеет более низкие значения, чем до индентирования. Было показано, что это связано с образованием полуметаллических фаз Si-III/Si-XII и аморфного кремния более высокого давления в результате ползучести материала при длительно действующем давлении. Чем продолжительнее время выдержки под нагрузкой, тем большее понижение электрического сопротивления наблюдается в области отпечатка, за исключением времени выдержки более 1 часа, что объясняется замедляющейся скоростью ползучести кремния для этого временного интервала, ведущей к остановке дальнейшего распространения зон аморфного и Si-III/Si-XII кремния, обладающих меньшим электрическим сопротивлением.