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Study of nanostructured layers of single-crystal silicon by scanning tunnel spectroscopy

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The nanostructured silicon surface has been studied using the scanning tunnel microscopy and spectroscopy in air. The local density of electron states was defined as normalized differential tunnel conductivity $(dI/dU)/(I/U)$. The surface morphology has been found to be characterized by the presence of a homogeneous nanostructure on the initial substrate microrelief. For the first time it has been shown that the spectrum of electron states changes considerably during the growth of a nanostructured silicon film.

Методом сканирующей туннельной микроскопии и спектроскопии на воздухе исследована поверхность наноструктурированного кремния. Локальная плотность электронных состояний определялась как нормированная дифференциальная туннельная проводимость $(dI/dU)/(I/U)$. Установлено, что морфология поверхности характеризуется наличием однородной наноструктуры на поверхности исходного микрорельефа подложки. Впервые показано, что в процессе роста пленки наноструктурированного кремния спектр электронных состояний существенно изменяется.

The development of nanotechnologies stimulates a huge interest in studies of nanostructured materials, due to the unique physicochemical properties thereof. So during formation of nanostructured silicon (ns-Si) on single-crystal silicon substrates, changes occur not only in structural properties, resulting in changed band gap width and appearance of quantum size effects, but also in formation of new compounds on the silicon surface with increased content of hydrogen and amorphous silicon. Last years, a considerable attention is focused on research of photo- and electroluminescence properties of nanostructured silicon and use of that material in such areas as biotechnology, gas detectors, etc. [1–5]. At the same time, a great attention is also given to development of methods to control and manage the parameters of nanosized materials with the aim to stabilize their characteristics. Of a special interest from the viewpoint of practical use of nanostructured silicon layers in microelectronics is the problem of electron state spectrum as of a spatially variable characteristic, which was not considered in the literature till now. It is known that information on local density of states near to the Fermi level can be obtained in experiment using scanning tunnel spectroscopy. In this method, both density of occupied and free states (valence

band and conduction band) is probed, the band gap width can be determined, too [6]. The task of this work was to measure the local density of states in nanostructured silicon layers using the scanning tunnel spectroscopy in air and to determine the extent of the changes in the local density of states depending on thickness of the studied layers.

We have used boron doped single-crystal silicon square wafers with resistivity of 1 Ω·cm, of 100 cm^2 area and 0.3 mm thickness. The surface of the wafers was not polished. The ns-Si layers were prepared by etching in $HF:HNO_3$ solution at room temperature, natural day-time illumination and time duration from 1 to 20 min. The nanostructural silicon layer thickness was varied from 3 up to 60 nm, controlled by technological process parameters of chemical modification of the single-crystal silicon surface and determined using the Auger electron spectroscopy. To study the surface morphology and access the characteristic sizes of the layer structure, the scanning tunnel microscopy was used. The tunnel current-voltage characteristics were measured in air using a scanning tunnel microscope in the bias voltage range between a probe and sample from −8 up to +8 V, with the positive voltage corresponding to positive potential on the sample. As a probe, a platinum nib was used. The measurements were carried out at a constant gap. The repeated measurements of current-voltage characteristics in each point at different areas of the nanostructured silicon layer surface were carried out. The averaged current-voltage characteristics (from 50 measurements) were smoothed out additionally using a the Fourier filter, and normalized differential conduction $(dI/dU)/(I/U)$ was calculated. According to [6], the dependence $(dI/dU)/(I/U)$ on the bias voltage reflects the distribution of electron state density in energy $E = eV$ (e is the electron charge), thus $U = 0$ corresponds to the Fermi level (E_F), the negative biases correspond to occupied states ($E<E_F$), while the positive biases, to free states ($E>E_F$).

Study of the surface morphology by the scanning tunnel microscope has shown that ns-Si has an ordered structure and repeats exactly the surface morphology of the single-crystal silicon substrates, forming pores on every single relief piece (Fig. 1). To study the local density distribution of electron states on the surface of ns-Si layer, the samples with different thickness of nanostructured silicon from 3 nm up to 60 nm were used. The obtained current-voltage characteristics have shown that variation of the current-voltage characteristic depending on thickness of ns-Si layer is non-linear. The characteristic dependences of the normalized differential conductivity $(dI/dU)/(I/U)$ on the bias voltage U for ns-Si layers are given in Figs.2 through 4. The edge of occupied states and edge of free states (conditionally valence band and the conduction band) can be easily observed. Approximating straight lines to the right and to the left of a Fermi level have the same slope. The latter evidences that the electron state distributions in energy at $E<E_F$ and $E>E_F$ are identical (Fig. 2–4). Displacement of the Fermi level (E_F) with respect to the band edges is also observed. So, for curve of Fig. 2, the Fermi level is shifted to the valence band edge, and for curve of Fig. 3, to the conduction band edge. Thus, the of electron state spectrum for ns-Si layers of various thickness changes essentially.

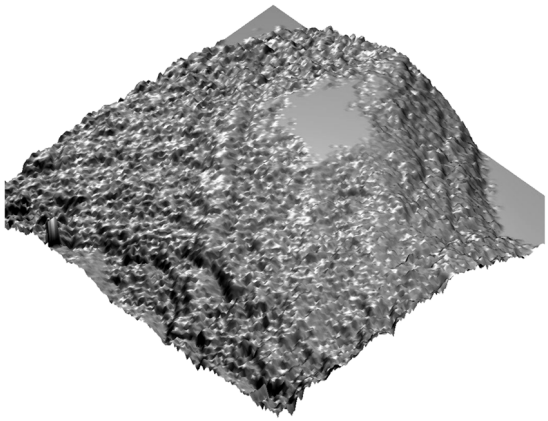

Fig. 1. Scanning tunnel microscope image of the ns-Si surface, the scanned area is 1×1 μm^2.

Despite of distinctions in typical spectra of normalized differential conductivity presented in Fig. 2–4, it is possible to reveal a number of common regularities for studied ns-Si layers. In the field of negative bias ($E<E_F$), sharp change in $(dI/dU)/(I/U)$ is seen in curves of Fig. 2 and Fig. 4 which can be ascribed to the valence band edge. Moreover, the crossing of conditional approximating straight line with the line $(dI/dU)/(I/U) = 0$ for those curves gives close values of a voltage cut-offs, about −1 V. It means that there is an obvious trend to a steady arrangement of the Fermi level at energy ~1 eV higher than the valence

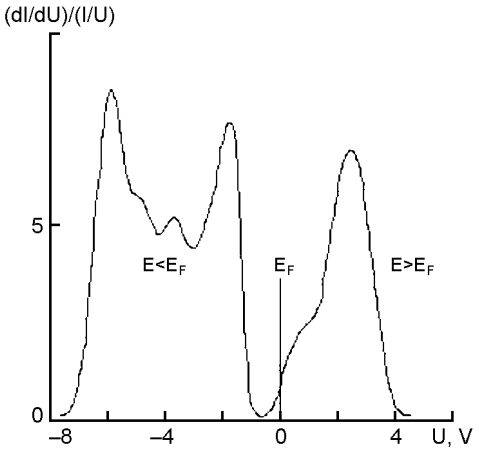

Fig. 2. Normalized differential conductivity as a function of bias voltage obtained from averaged current-voltage characteristic, for ns-Si layer (3 nm).

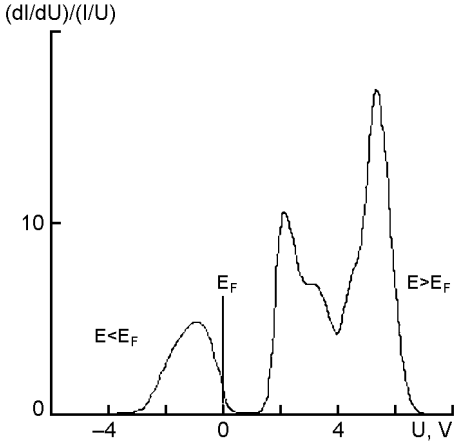

Fig. 3. Normalized differential conductivity as a function of bias voltage obtained from averaged current-voltage characteristic, for ns-Si layer (9 nm).

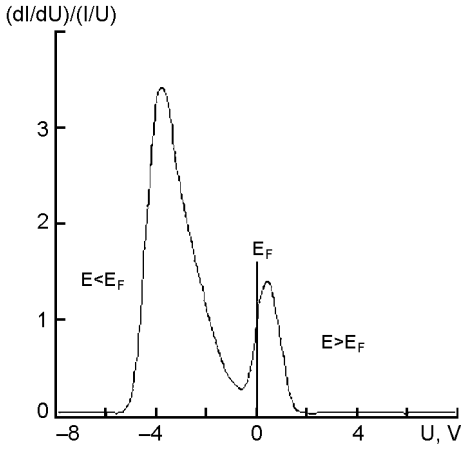

Fig. 4. Normalized differential conductivity as a function of bias voltage obtained from averaged current-voltage characteristic, for ns-Si layer (60 nm).

band edge. At the same time, in the field of positive bias ($E>E_F$) in the curve of Fig. 3, a sharp $(dI/dU)/(I/U)$ change is also observed which can be ascribed to the conduction band edge. The crossing with the line $(dI/dU)/(I/U) = 0$ for this curve gives a close value of a voltage cut-off, about +1 V. The Fermi level for ns-Si layers curve (Fig. 3) is somewhat closer to the valence band rather than to the conduction one, thus showing some prevalence of *p*-type conductivity in these ns-Si layers. While for ns-Si layers of other thickness values, the Fermi level is located somewhat closer to the conduction band rather than to valence one (Figs. 2, 4), thus evidencing some prevalence of *n*-type conductivity. Thus, an obvious trend to conductivity type change is observed during formation of ns-Si layer depending on its thickness. At first, the *n*-type conductivity is observed (Fig. 2). Then, when thickness of ns-Si layer reaches 9 nm, the *p*-type conductivity is observed. Further, at thickness exceeding 18 nm, the *n*-type conductivity is observed again.

Thus, the ns-Si layers behave as homogeneous films in measurements of electron state local density. The general picture of electron state local density in the layers is as follows. The valence band edge (sharp change of electron state density at $E<E_F$) is revealed in most obtained spectra. At $E>E_F$, the energy dependence of electron state density is of a different kind, but more often it is possible to interpret this wide smooth distribution without sharp changes as the conduction band edge. Only occasionally there are spectra where both valence band edge and the conduction band edge are observable clearly. The change of conductivity type in the formed ns-Si layers is observed depending on their thickness.

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Вивчення наноструктурованих плівок монокристалічного кремнію методом сканувальної тунельної спектроскопії

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Методом сканувальної тунельної мікроскопії та спектроскопії на повітрі досліджено поверхню наноструктурованого кремнію. Локальна щільність електронних станів визначалася як нормована диференціальна тунельна провідність $(dI/dU)/(I/U)$. Встановлено, що морфологія поверхні характеризується наявністю однорідної наноструктури на поверхні мікрорельєфу підкладки. Вперше показано, що у процесі росту плівки наноструктурованого кремнію спектр електронних станів істотно змінюється.