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PHOTO-EMF PECULIARITIES OF Ge NANOCLUSTER STRUCTURES FORMED ON OXIDIZED Si SURFACE

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Ge nanocluster systems on SiO_x are paid much interest of scientists today as far as introduction of an insulting SiO_x layer can modify essentially the electrical properties of well examined Ge on Si structures making such systems prospective in the view of their possible application to new nanoelectronic devices such as memory cells, solar elements, and infrared photodetectors. A possibility of epitaxial formation of Si and Ge nanoclusters on initially amorphous silicon oxide layer is considered. The effect of such a layer on the density and uniformity distribution of the self-assembled Ge nanoclusters formed in molecular-beam epitaxy chamber "Katun" on SiO_x ($x \leq 2$) and their optoelectronic properties, in particular lateral photoconductivity and photo-emf, has been investigated.

EXPERIMENTAL SAMPLES AND EPITAXIAL FORMATION

The experimental samples with Ge nanoclusters were prepared by molecular-beam epitaxy (MBE) on initially amorphous silicon oxide layer. At first the substrate was chemically cleaned, when the natural oxide layer was removed from the surface and a thin passivating oxide layer of the thickness 1–2 nm was formed. The substrate was thermically cleaned at the temperature 800°C in the MBE chamber under the conditions of super high vacuum ($<10^{-8}$ Pa). Then the germanium flux was directed to the surface at the temperature 700–750 °C. The surface reconstructions were controlled by RHEED for all the stages of Ge nanoisland formation [3]. At first diffusion background with central reflex and Cicucci lines was observed corresponding to amorphous SiO_x layer. When first reflexes appeared, it testified that the formation of three-dimensional nuclei of nanoclusters started. As further Ge exposition went on, the order of reflexes increased testifying that Ge nanocluster grew larger. Then the main difference of Ge on SiO_x from the case of Si epitaxy on SiO_x is that no nanoisland facets were formed and they did not grow together making a continuous monocrystalline film Si (100) like that in the case of Si superstructure (2×1) [3].

Ge nanoclusters were about 1–2 nm in height and 10–20 nm in the basis for the initial stage of their formation with a low distribution density about 10^8 cm^{-2} (Fig. 1). As the epitaxial growth went on for other samples, Ge nanoclusters grew larger: about 20 nm in height and 150 nm in the basis with the density distribution over the substrate surface varying from 10^8 to 10^{11} cm^{-2} depending on the parameters of epitaxial growth. These nanoclusters revealed no facets and seemed to be amorphous or polycrystalline.

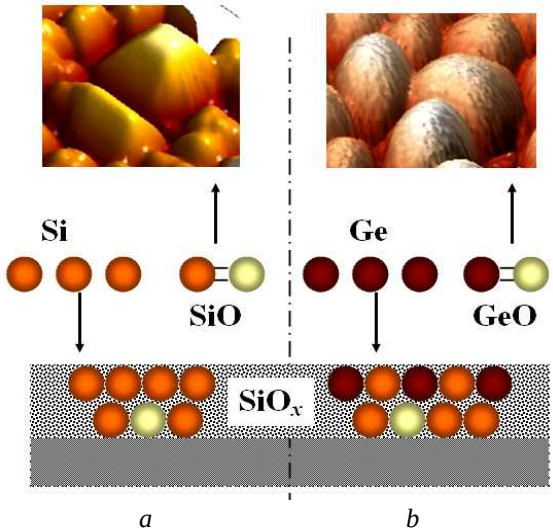

Fig. 1. Epitaxial formation of Si nanoclusters (*a*) and Ge nanoclusters (*b*) on initially amorphous Si(100) surface

The formation of Ge nanoclusters on SiO_x differs from traditional heteroepitaxial growth of Ge quantum dots on Si (100) by Stranski-Krastanow mechanism where elastic deformation between Si

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and Ge plays the key role in nanocluster formation [4], or epitaxial growth of Si nanoclusters on SiO_x [3], which seem to show monocrystalline features: {113} side facets with characteristic angles of about 25 ° and top (100) terraces that correspond to Si (100) epitaxial formation, despite the presence of initially amorphous oxide layer.

It is interesting, whether SiO_x intermediate layer really remains, after the substrate surface was thermically cleaned heated to the temperature 750°C. To discover this question, we tried Auger-spectroscopy of the silicon substrate covered with passivating silicon oxide layer (2–5 nm) after chemical cleaning before heating and after the heating at 900 °C during one hour. We can see that the peak corresponding to SiO_2 remains at the surface after the heating showing the presence of a thin SiO_2 layer of the thickness about 1–2 nm.

To understand the growth mechanism of Ge nanoislands on SiO_x, let us consider at first Si epitaxy on SiO_x film. We suppose that the processes on the surface can be described by the following reactions [3]. In this case the surface cleaning goes by liftoff the fragment SiO from the surface at $1 < x < 2$: $SiO_x + Si \rightarrow SiO_{x-1} + SiO\uparrow$ or the chemical heterogeneity can be healed by incorporation of Si atom into the silicon oxide lattice at $1 < x < 2$: $SiO_x + Si \rightarrow 2\,SiO_{x/2}$. In such a way, the centres of silicon nanocluster crystallization are created on the surface. It happens that the SiO_x oxide layer is depleted from both sides – from the substrate side due to diffusion of O up and from above one due to reaction between oxygen and incoming Si atoms.

In the case of Ge epitaxy on SiO_x the situation is quite different: we have two lattices – Si and Ge leading to deformation between them. Oxygen atoms make the surface even more inhomogeneous. But we can also consider the same reactions at the surface: the surface cleaning goes by liftoff a fragment GeO or SiO from the surface or incorporation of Ge atoms into the lattice occurs: $SiO_x + Ge \rightarrow SiGeO_x$. Due to elastic deformation between Si and Ge, the surface is very inhomogeneous. The incoming Ge atoms migrate by the surface occupying the places corresponding to minimum of the total surface energy. At the initial stages, nanoclusters can be formed locally by Volmer-Weber growth mode, when the wetting SiGe layer was not yet formed, and then the growth goes by Stranski-Krastanow mode, since a lattice mismatch exists between $SiGeO_x$ and Ge. The presence of oxygen even of a very little concentration may essentially influence on deformation relaxation. The effect of H is not clear. The monocrystalline epitaxial growth may occur in certain local positions, but since their relative orientation is random, Ge nanoclusters can be polycrystalline or amorphous and are almost hemispherical.

PHOTOELECTRONIC PROPERTIES

The question is how the additional intermediate SiO_x layer affects photoelectrical properties of Ge nanocluster structures, in particular lateral photoconductivity. To answer this question, we studied photoconductivity spectra of heterostructures with Ge nanoclusters of different morphology, in particular nanocluster size and distribution density.

The structures with different morphology of Ge nanoislands appeared to show different photosensitivity values [5]. It was revealed that at the room temperature the lateral photocurrent in the range $h\nu > 1.05$ eV for the samples with little number of Ge nanoislands on SiO_x is similar to the spectrum obtained for the structures with crystalline Ge quantum dots on Si (Fig. 2). At the same time, for the sample with large number of Ge nanoislands an essential drop of photocurrent was observed in the range $h\nu > 1.05$ eV and a photocurrent generation in the range of smaller quanta energy $h\nu \sim 0.55$ eV where crystalline Si is transparent.

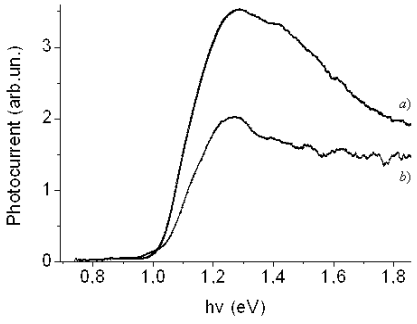

Fig. 2. Spectral dependences of lateral photoconductivity of Ge-SiO_x-Si heterostructures with different density distribution of the nanoislands at 290 K and U = 5 V: ~10^8 cm^{-2} (*a*); ~10^{10} cm^{-2} (*b*)

Even more pronounced difference in the photocurrent was observed for the samples measured at 77 K (Fig. 3). In the structure A with little number of Ge nanoislands, the lateral photocurrent was observed starting from $h\nu > 0.8$ eV. In contrast, the structure B with large number of Ge nanoislands showed essential photosensitivity for quanta energy 0.55 eV where

crystalline silicon is transparent. Thus, the absorption edge appeared to be shifter corresponding to 0.55 eV while the band gap energy of crystalline Ge is of 0.67 eV [6].

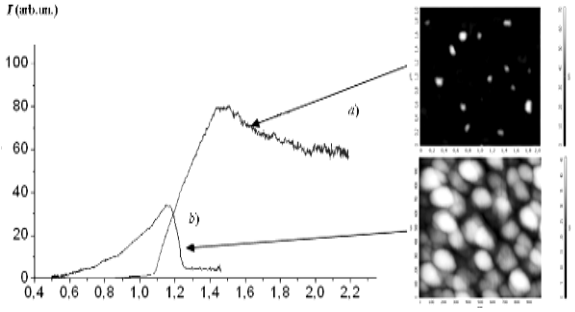

Fig. 3. Spectral dependences of lateral photoconductivity of Ge-SiO_x-Si heterostructures with different distribution density of the nanoislands at 77 K and U = 5 V: ~10^8 cm^{-2} (*a*); ~10^{10} cm^{-2} (*b*)

So, we observed essential difference in photosensitivity of the two structures that differ in the number of Ge nanoislands or in the total surface covered by Ge nanoislands. This effect is much more pronounced at low temperature. This suggests that Ge nanoislands makes this effect. And we should consider the influence of them, in particular, on transitions involving localized states in the nanoislands.

We suppose that Ge nanoislands, both amorphous or polycrystalline, are centres capturing holes as far as traditional (Ge on Si) ones are considered to be the second type heterostructures [7]. The positive charge value captured by one nanoisland is proportional to its capacity. Consequently, the larger are islands, the larger charge they capture. The electric field created by this positive charge of the nanoislands separated from p-type Si substrate by a thin SiO_x layer depletes the surface layer of p-Si and influences essentially the recombination processes and carrier transport as well as lateral photoconductivity in the range at $h\nu > 1.05$ eV. It is known that absorption coefficient in amorphous semiconductors is several orders higher than that in the same crystalline materials, as far as phononless direct transitions become possible in amorphous disordered material [8]. If we consider amorphous Ge for quantum energy 0.5 eV, the absorption coefficient is $\alpha = 10^2$ cm^{-1}, and for $h\nu = 1.2$ eV $\alpha \sim 10^5$ cm^{-1} what is several orders higher than those in crystalline Si and Ge [7]. So, it appears that a very thin amorphous Ge layer of the thickness about 15 nm may absorb up to 10 % of light in the range 0.5–1.0 eV, where crystalline Si is transparent. This fact explains the difference in photocurrent values for two structures we for two structures we considered. All the absorption goes in Ge nanoislands themselves.

So we should consider transitions in the nanoislands. The carriers in the nanoislands are localized and cannot participate in the carrier transport. To contribute to the photocurrent, a thermical generation is required with further tunneling to the near-surface Si layer via SiO_x layer. In such a way, for lower energies we consider transitions from localized states of Ge nanoislands and we have extrinsic photoconductivity. For higher energies $h\nu > 1.05$ eV we consider interband transitions. In this situation it is very important that these nanoislands are amorphous. When we consider an amorphous material, instead of the energy gap in crystalline material there will be a quasigap, where the density of states is not zero and there are no sharp edges of the bands. The states in the quasigap are believed to be localized. As the temperature decreases, the Fermi level is shifted in the direction of the valence band of Si, leading to the corresponding shift of the low-energy edge of the photoconductivity spectrum to IR range. Doing so, the Fermi level passes through the area of higher density of states. As a result, the photocurrent value increases. This explains why the low-energy edge of photocurrent spectrum is shifted to lower temperatures, as the temperature of measurement decreased. In addition, the photo-emf efficiency seems to depend essentially on Ge nanocluster density distribution and the presence of SiO_x layer that causes noticeable increase in the photo-emf efficiency for several structures with Ge NCs on SiO_x [9]. A nature of this effect can be attributed to formation of confined states at the interface of isolating SiO_x layer that are capture centres for holes and electrons reducing recombination rate. This assumption is confirmed by the observation of a hysteresis of voltage-capacitance characteristics measured in such structures.

CONCLUSIONS

Formation mechanism of epitaxial heterotructures with Ge nanoislands on SiO_x film and their optical properties have been investigated. It has been revealed that Ge on SiO_x nanoisland structures shows higher photoresponce in the mid-IR range as compared to that of Ge/Si heterostructures. Increasing of surface density of Ge nanoislands leads to increasing of photovoltage and photocurrent signal in the IR range. We suppose that accumulation of charge carriers by nanoislands shows an effect on surface potential fluctuation and photosensitivity value. In such a way, the

value. In such a way, the introduction of a superthin SiO_x layer and fitting corresponding parameters can essentially enlarge the area of their application to nanoelectronic devices or improve their efficiency.

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Особливості фото-ерс нанокластерних структур Ge, утворених на оксидованій поверхні Si

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Досліджено вплив первісно аморфного шару SiO_x на морфологію та оптоелектронні властивості систем нанокластерів Si та Ge, одержаних методом молекулярно-променевої епітаксії. Запропоновано механізм формування нанокластерів при взаємодії надкритичних потоків германію чи кремнію з первісно аморфною поверхнею, який базується на заліковуванні хімічної неоднорідності та вбудовуванні атомів Si в SiO_x, а також виникненні напружень внаслідок невідповідності сталих граток. Для того, щоб переконатися, яким чином наявність додаткового проміжного субмоношару SiO_x впливає на фотоелектричні властивості структур з нанокластерами Ge, досліджено спектри фотопровідності та фото-ерс таких систем і порівняно з раніше одержаними спектрами традиційних структур Ge на Si.

Особенности фото-эдс нанокластерных структур Ge, образованных на оксидированной поверхности Si

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Исследовано влияние первично аморфного слоя SiO_x на морфологию и оптоэлектронные свойства систем нанокластеров Si и Ge, полученных методом молекулярно-лучевой эпитаксии. Предложен механизм формирования нанокластеров при взаимодействии сверхкритических потоков германия или кремния с первоначально аморфной поверхностью, который основывается на залечивании химической неоднородности и встраивании атомов Si в SiO_x, а также возникновении напряжений из-за несоответствия постоянных решеток. Для того, чтобы выяснить, каким образом наличие дополнительного промежуточного субмонослоя SiO_x влияет на фотоэлектрические свойства

структур с нанокластерами Ge, изучены спектры фотопроводимости и фото-эдс таких систем и сопоставлены с ранее полученными спектрами традиционных структур Ge на Si.