Observation of 2D-exciton luminescence in germanium layers in periodic Ge–$Ge_{1-x}Si_x$ heterostructures

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The photoluminescence in strained periodic Ge–$Ge_{1-x}Si_x$ heterostructures with nanometer-thickness layers has been studied. Below 90 K, the observed emission results from a recombination of 2D excitons in the germanium layers.

Excitons and the associated recombination radiation in indirect-gap semiconductors, in particular, silicon, and their solid solutions, are of research interest in connection with the problem of phase transitions of a gas of excitons to a condensed state. The set of effects which arise from the condensation of an exciton gas into an electron–hole liquid has so far been studied primarily in homogeneous bulk materials.[1] In this case, the effects are manifested at fairly high levels of the optical excitation and at relatively low temperatures. When we move to 2D systems, we find that the binding energy of the electron–hole pair increases, so collective effects can be studied under much less severe conditions.[2] It becomes possible to observe some subtle interactions associated with the formation of both a 2D electron–hole liquid and 2D-exciton molecules.

Two-dimensional excitons in germanium have been studied in the channels at the boundary between a bulk semiconductor and an electrolyte. The electrons and holes bound in pairs lay at some distance from each other (in real space) and formed a charge double layer near a semiconductor–electrolyte heterojunction.[3] Other promising systems for a study of phase transitions of 2D excitons of germanium are heteroepitaxial Ge–$Ge_{1-x}Si_x$ structures.[4] When the germanium layers in these structures are thin, one can induce a transition from purely 2D to quasi-2D systems by varying the thickness of the layers of solid solution.

In this letter we are reporting the first observation of a 2D-exciton luminescence in thin (8–25-nm) layers of germanium of periodic Ge–$Ge_{1-x}Si_x$ heterostructures grown on Ge [111] substrates. The Ge layers in the heterostructures were separated by tunneling-opaque layers of the solid solution $Ge_{1-x}Si_x$ ($x<0.15$) with a thickness of 20–30 nm. They formed potential wells for both electrons and holes. The number of periods ranged from 70 to 300 for the various structures; the total thickness of the superlattices studied was 3–15 μm. At this thickness we could rule out a contribution of the substrates to the photoluminescence spectra. The structure and electrical properties of the superlattices studied here are described in more detail in Ref. 5.

The photoluminescence was studied in the temperature range 2–300 K on a BOMEM DA3.36 Fourier spectrometer equipped with cooled InSb detector. For excitation we used the beam from a Nd:YAG laser ($\lambda=1.06$ μm). The shape of the

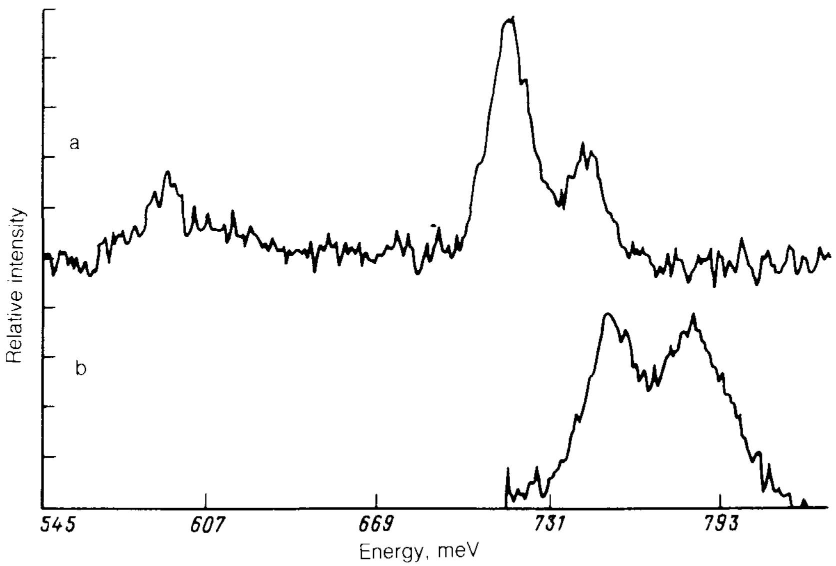

FIG. 1. Photoluminescence spectra of Ge–$Ge_{1-x}Si_x$ superlattices.

luminescence spectral lines was corrected on the basis of the emission from a blackbody. Figure 1 shows typical photoluminescence spectra for samples with $d_{Ge}=21$(a) and 11 nm (b), $d_{GeSi}=29$(a) and 18 nm (b), $x=0.12$(a) and 0.14 (b), $N=73$ periods (a) and 200 periods (b), and $\xi=25\%$ (a) and 28% (b). The latter percentages are measures of the elastic effect of the substrate on the superlattice.[6] The spectra were recorded at $T=5$(a) and 80 K(b); the intensity of the laser light was $I_{excit}=15$ W/cm^2. The resolution was 0.4 meV.

There are several spectral lines here in the region 550–800 meV at $T<90$ K. The peak near 600 meV (2.1 μm) is usually linked with dislocations. The second peak in the luminescence, whose position varies with the extent of elastic deformation and the thickness of the germanium layers in the superlattice (Fig. 1, a and b), stems from the recombination of an exciton involving an LA phonon in Ge. In the superlattices with thick (>20 nm) Ge layers, the position of this peak is close to that of the corresponding line in bulk Ge (714 meV at $T=4.2$ K; Fig. 1a). The high-frequency peak corresponding to an energy of 735 meV in the superlattice with thick germanium layers is displaced with respect to the LA-exciton replica. The magnitude of this displacement is equal to the energy of a longitudinal acoustic phonon. This peak is caused by a nonphonon recombination of indirect excitons associated with scattering by impurities in the germanium layers.[7] The background impurity concentration in the Ge and $Ge_{1-x}Si_x$ layers of the heterostructures studied is estimated to be $\sim 10^{14}$–10^{15} cm^{-3}.

In Fig. 2 we use the example of the photoluminescence spectra of a superlattice with $d_{Ge}=18$ nm, $d_{GeSi}=30$ nm, $x=0.13$, $N=243$, and $\xi=12\%$ to show how the

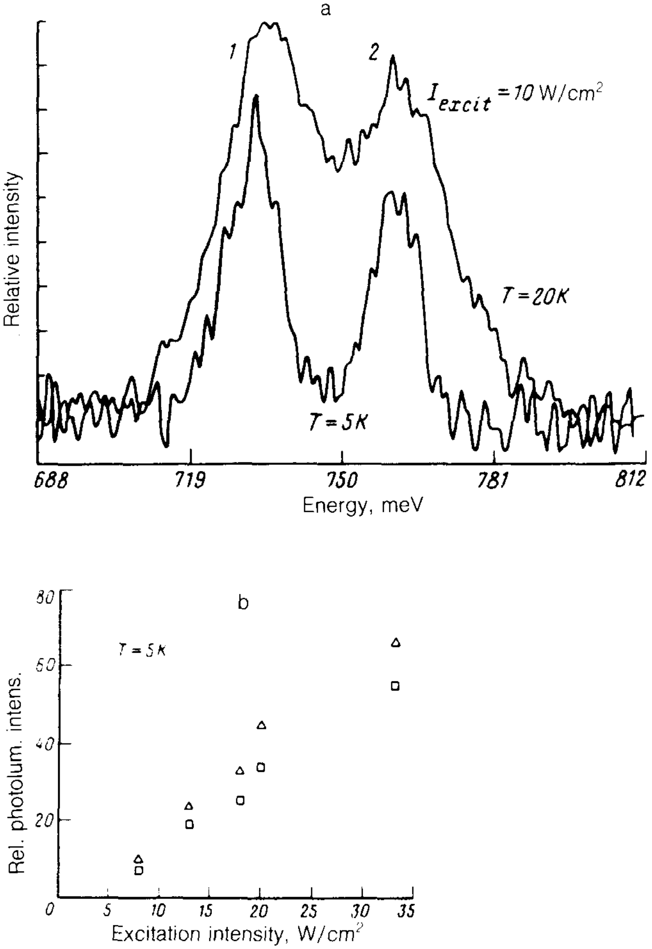

FIG. 2. a—Shape of the photoluminescence lines versus the temperature; b—intensity of the photoluminescence lines versus the intensity of the exciting radiation.

shape of the *LA* replica (1, Δ) and that of the nonphonon replica (2,□) vary with the temperature (a) and how the intensity of the replicas varies with the laser intensity (b), at $T=5$ K. The characteristic temperature dependence of the shape of the lines in the spectrum and the linear dependence of the amplitudes of the *LA* and nonphonon replicas on the laser intensity indicate that the photoluminescence peaks which we observe in the periodic Ge–$Ge_{1-x}Si_x$ heterostructures correspond at $T \geqslant 5$ K to a recombination of free excitons in the system. The broadening of the spectral lines with increasing temperature occurs mostly in the short-wave direction. This circumstance is characteristic of a system of free excitons; it stems from a dependence of the emission spectral line on the energy distribution of the excitons.

We also observed *LA* and nonphonon replicas of excitons bound by impurities.

These replicas are less intense than the photoluminescence peaks of free excitons. Because of the large widths of the free-exciton lines (the average value is on the order of 15 meV at $T=5$ K and at a laser intensity $P=5$ W/cm^2, in comparison with the corresponding figure of 3.5 meV for the *LA* peak of bulk germanium, measured under the same conditions), the emission lines of bound excitons are resolved only at lower temperatures ($\leqslant 4.2$ K). The broadening of the exciton lines is apparently due to a scatter in the thicknesses of the Ge layers of the superlattice. The validity of this conclusion will be demonstrated below. In the luminescence spectra of the thick (>1 μm) autoepitaxial Ge layers, bound excitons are also detected at $T=5$ K.

In autoepitaxial layers of Ge with a background impurity concentration $N \leqslant 10^{14}$ cm^{-3}, only well-defined *LA* replicas of free and bound excitons are observed at $T \simeq 5$ K. The *TA* and nonphonon exciton replicas are poorly defined. In Ge layers autodoped to a level $N \sim 10^{15}$ cm^{-3}, a nonphonon replica comparable in intensity to the *LA* replica appears in the photoluminescence spectra (at the same temperatures). In a Ge–Ge$_{1-x}$Si$_x$ superlattice, the level of uncontrolled impurity atoms in the Ge layers is greater than that in autoepitaxial layers of germanium. This circumstance explains the high intensity of the peaks of nonphonon transitions in the luminescence spectra of the superlattices.

The temperature dependence of the photoluminescence intensity, which generally shows a decrease in intensity with increasing temperature at a fixed intensity of the exciting light, reaches a peak at $T=15$–20 K. The increase in the emission intensity with the temperature in the interval 4–20 K stems from an escape of some of the excitons captured by impurity centers to a free state. With a further increase in the sample temperature, the photoluminescence intensity decreases. However, the structure of the exciton lines in the spectra (Fig. 2a) can be resolved at temperatures to ~ 85–90 K (which we call $T_{\max}$), despite the pronounced broadening of these lines.

The significant exciton binding energy in the germanium layers of Ge–Ge$_{1-x}$Si$_x$ superlattices makes it possible to study them at temperatures above liquid-nitrogen temperatures (Fig. 1b). This binding energy indicates that the observed excitations are two-dimensional. From their temperature dependence we can estimate the exciton binding energy in a superlattice, $E_{\text{excit}} \sim k_B T_{\max} \simeq 8$–$9$ meV (k_B is the Boltzmann constant). This figure is about 2-2.5 times the exciton binding energy in bulk germanium (~ 4 meV). Theoretical exciton binding energies in the strained Ge layers of a superlattice are close to our estimate.

Figure 3 shows how the positions of the *LA* (Δ) and nonphonon (square) replicas of free excitons in the photoluminescence spectra vary as the layer thickness d_{Ge} in the superlattice is increased. The parameter values for points 1–5, respectively, are as follows: $d_{\text{Ge}}=8.5$ nm, 11, 18, 21, and 22.5 nm; $d_{\text{GeSi}}=26$ nm, 18, 30, 28, and 22.5 nm; $x=0.15$, 0.14, 0.13, 0.12, and 0.12; $N=81$, 90, 243, 73, and 81; $\xi=17\%$, 28%, 12%, 25%, and 36%. With decreasing width of the potential wells in the superlattice, the photoluminescence peaks undergo a pronounced displacement up the energy scale. According to the theory (Ref. 6, for example), the shift of the edges of the energy bands in Ge layers of a Ge–Ge$_{1-x}$Si$_x$ heterostructure, due exclusively to elastic deformation, occurs in the direction which reduces the width of the band gap.

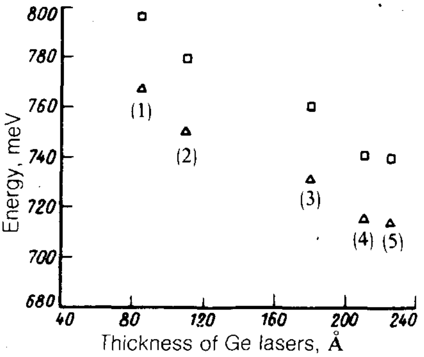

FIG. 3. Positions of the photoluminescence lines of the free excitons for superlattices with various widths of the Ge quantum wells.

We observe this effect, in particular, in thick heteroepitaxial layers of Ge grown on a Ge$_{1-x}$Si$_x$ buffer.

An *increase* in the width of the band gap in thin Ge layers of a heterosystem could result only from a quantum-size effect in the carrier spectrum in the layers of the structures. It has been shown previously[8,9] that a quantization of the energy spectrum of holes, which localize in potential wells formed by the germanium layers of the superlattice, does indeed occur in these heterostructures. Since the upper states of the valence band are filled by heavy holes with a mass $m_h^{\perp}=0.13m_0$ (m_0 is the mass of a free electron) across the plane of the layer, to estimate the position of the first quantum-size level we can use the model of an infinite square well. For a Ge layer ~ 10 nm thick we then find that the upper quantum-size level must undergo a shift of $\simeq 25$ meV with respect to the edge of the valence band of 3D germanium. This shift is much smaller than the shift of the photoluminescence peaks observed experimentally ($\Delta E \simeq 60$ meV). The difference in energy can be attributed to a quantum-size effect in the electron spectrum.

In the germanium layers of Ge–Ge$_{1-x}$Si$_x$ superlattices which have been subjected to a radial compression in the plane of the layers of the system, the intervalley degeneracy in the conduction band is lifted. As a result, a valley which lies on the [111] axis of the superlattice, and which has a heavy effective electron mass ($m_e^{\perp,(1)}=1.58m_0$) across the plane of the layers, is shifted $\simeq 60$ meV upward as a result of the deformation.[6] The electrons of the three other valleys, which form the bottom of the conduction band in thick Ge layers, have a smaller effective mass across the Ge layer ($m_e^{\perp,(3)}\simeq 0.09m_0$). The quantization of the electron spectrum in these valleys causes a shift of $\simeq 35$ meV of the edge of the conduction band, leading to an additional increase in the width of the band gap and therefore a shift of the lines in the photoluminescence spectrum toward shorter wavelengths. The agreement between the theoretical predictions and the experimental shifts of the photoluminescence peaks indicates a quantization of the electron spectrum in the germanium layers of the Ge–Ge$_{1-x}$Si superlattices.

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