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The 2D conducting system formed by nanocrystallites $CrSi_2$ in the (111) plane of silicon: New object

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HIGHLIGHTS

- The activation energy is lower than in the case of impurity condition.
- The carrier mobility is very high but it decreases rapidly with the growing temperature.
- The magnetoresistance is linear and decreases rapidly as the temperature rises.

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ABSTRACT

A conductivity quasi-two-dimensional system formed by nanocrystallites $CrSi_2$ located in the crystallographic (111) plane of silicon has been considered. At low temperatures the system exhibits several unique properties: (i) the activation energy in the temperature dependence of resistance is appreciably lower than in the case of impurity condition; (ii) the carrier mobility is very high but it decreases rapidly with the growing temperature; (iii) the magnetoresistance is linear and decreases rapidly as the temperature rises. To explain these features, a model has been proposed which assigns special importance to the charges at the nanocrystallites which appear due to the escape of the electrons to the conduction band (or holes to the valence band) of silicon.

The present technologies of materials for microelectronics have led to the advent of semiconducting single crystals in which impurity atoms are located within one crystallographic plane (the so-called δ-layers). These types of structures possess two-dimensional conductivity as in heterojunctions or inversion layers. Nevertheless, δ-layers were little used in microelectronics mainly because of the low mobility of the carriers subjected to frequent scattering at the ionized atoms in the δ-layer [1]. Meantime a structure in which one crystallographic plane of a high-energy-gap semiconducting crystal contains nanodimensional crystallites, rather than individual atoms, can exhibit new interesting and practically significant properties. These expectations were essentially supported while investigating the electron properties of an object containing chromic disilicide nanocrystallites in the crystallographic (111) plane of silicon. The chromic disilicide $CrSi_2$ is a low energy gap semiconductor (E_g=0.32 eV) [2] used in optical electronic IR elements, thermoelectric devices and so on.

The detailed description of the sample preparation and characterization is given in Ref. [3]. The sample was prepared as follows.[1] The p-type Si(111) wafer was used as the substrate. The native oxide and residual contaminants were removed from Si substrates' surface in the ultra high vacuum chamber by direct current annealing at 650–700 °C for 10–12 h, cooling during 12 h and finally by flashing at 1200 °C. Chromium was deposited from annealed Ta-tubes onto an atomically clean silicon Si(111)7 × 7 surface with a rate about 0.017 nm/min (~ 1 Å in terms of monolayer thickness). Silicon layers were deposited from sublimation silicon source made as the rectangular silicon plate, which is heated up with direct current flow. Silicon overgrowth with deposition rate of 3–4 nm/min was carried out by molecular beam

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epitaxy. The obtained crystal was annealed at $T=750\,^{\circ}C$ to produce a solid-phase reaction. According to electron microscopy, the obtained samples contained small ($\sim$ 2–3 nm) and large (20–40 nm) $CrSi_2$ nanocrystallites; their heights being 2–4 nm. The average spacing between the small crystallites was $\sim$20 nm. The surface density was $\approx 2.5\times10^{11}$ cm^{-2} for the small nanocrystallites and $\approx 3\times10^{9}$ cm^{-2} for the large ones [4].

Such a sample possesses maximum permissible conduction anisotropy: at low temperatures it has no conduction in direction perpendicular to the plane with nanocrystallites and the conductivity is affected only through the plane containing nanocrystallites, i.e. it is actually the conductivity of a two-dimensional electron (hole) system.

We have investigated the temperature dependences of kinetic properties (resistance, magnetoresistance, and the Hall emf) in the interval 10–60 K. The sample with $CrSi_2$ nanocrystallites used for electric measurements was shaped as a double cross made of a narrow strip $\sim$ 1.5 mm wide and 9 mm long with aluminum contacts implanted into the $CrSi_2$ nanocrystallites rich layer by thermocompression. The measurements were performed at direct current. The magnetic field (up to 5 T) was excited with an automatic field-scan superconducting solenoid.

In the absence of magnetic field the observed temperature variations of the resistance ρ_{xx} exhibited the semiconducting type of behavior (Fig. 1). The dependences $\ln(\rho_{xx})$ vs. $1/T$ in Fig. 1 show to what extent the resistance variations follow the Arrhenius law in the course of activations in different temperature intervals:

$$\rho(T)=\rho_0\exp\left(\frac{E_i}{k_BT}\right). \tag{1}$$

We can separate three temperature intervals in which resistance, magnetoresistance and the Hall emf exhibit essentially different behavior. In region I (<20 K) the energy E_1 (solid line in Fig. 1) in Eq. (1) is very low ($\sim$ 0.9 meV at $I=10$ mkA). This suggests normal hopping conduction in this region: the electrons (or holes) localized near the nanocrystallites $CrSi_2$ jump between vacant states. Note that the hopping mechanism operates in the forbidden zone of silicon. The activation energy is $E_2=6.88$ meV in region II (20–40 K) (dashed line in Fig. 1) and decreases to $E_3=2.86$ meV (dotted line in Fig. 1) in region III (40–70 K).

These temperature intervals with strikingly low activation energies in terms of the Arrhenius law show that the transport of charge carriers is determined not only by thermal activation but also by a more complex process. It is surprising indeed that the activation energy E_3 in higher-temperature region III is significantly lower than the activation energy E_2 in low-temperature region II. Normally, the intensity of the activation process holds or even increases when the temperature rises.

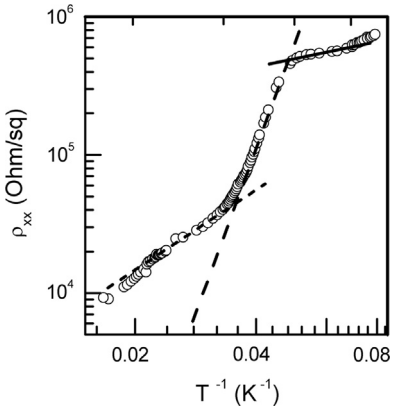

Fig. 1. The dependence of the sample resistance on opposite temperature T.

To obtain the temperature dependences of the carrier density n and mobility $\mu=e\tau/m^*$ (τ is the transport relaxation time, m^* is the effective mass), the Hall emf was measured at different temperatures. It was found that in all the cases the Hall emf changed linearly with the magnetic field. We could thus calculate the Hall constants for our two-dimensional system. The Hall constants, the carrier density n and the mobility μ were calculated within a two-dimensional model. In the equation for conductivity the parameters σ and n are related to unit area and the Hall constant is $R_H=U_{xy}/IB$, where I is the current and B is the magnetic field strength.

Note that the Hall constant of the investigated object varies in a very wide range: it decreases by three orders of magnitude (10^5–10^2 Ohm T^{-1}) as the temperature grows from 25 K to 60 K. The measured Hall constants show that the sample has hole conduction.

The parameters n and μ were calculated by standard equations for one type of carriers:

$$\sigma=ne\mu, \tag{2}$$

$$R_H=\frac{1}{ne}. \tag{3}$$

The density n is obtained from Eq. (3) and the mobility μ from Eq. (2) or from $\mu=\sigma R_H$. The dependences $n(T)$ and $\mu(T)$ are illustrated in Fig. 2a and b respectively. Note that the carrier mobility in region II is too high for such inhomogeneous sample.

Taking into account the dramatic temperature variations of the carrier mobility, the corresponding corrections must be made in the estimates of activation energy. For this purpose we can use the

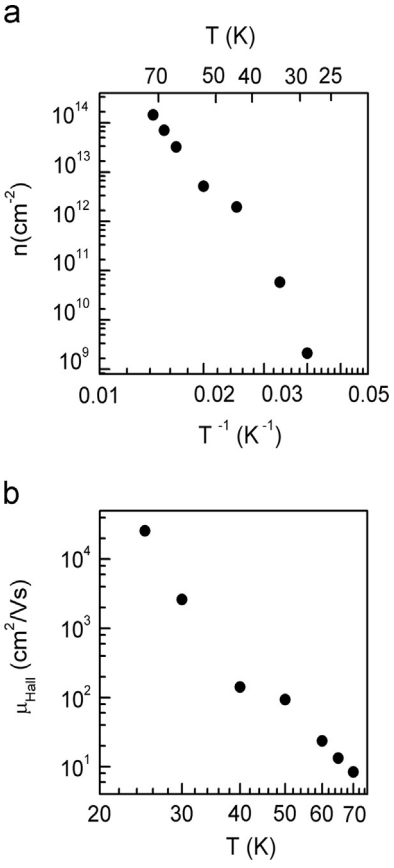

Fig. 2. The dependences of the carrier density n on T^{-1} (a) and the carrier mobility μ on $\ln(T)$ (b) (logarithmic scale along the ordinate axis).

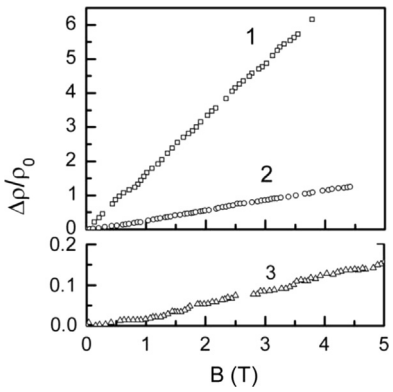

Fig. 3. The resistance variations $(\rho(B)-\rho_0)/\rho_0$ in the sample as a function of the magnetic field strength at temperatures: curve 1 is 25 K, curve 2 is 30 K, curve 3 is 40 K.

equation distributing directly the concentration variation:

$$n(T) = n_0 \exp\left(\frac{E_i}{k_B T}\right). \quad (4)$$

According to Eq. (4), E_i is $E_2 = 17$ meV in region II and $E_3 = 6.8$ meV in region III. When the dependence $\mu(T)$ is excluded from the conductivity, the activation energy increases 2.4 times.

The variation of resistance in a magnetic field is another surprising feature of the kinetic properties of the simple. In region II magnetoresistance $(\rho(B)-\rho_0)/\rho_0$ is a linear function of the magnetic field strength (Fig. 3). At $T=25$ K magnetoresistance (MR) is strikingly high but it decreases rapidly at the temperature rises.

Thus, the investigated object exhibits several extraordinary kinetic electron properties: (i) it has strikingly low activation energy in terms of the Arrhenius law which decreases further with the lowering temperature; (ii) the calculated carrier mobilities are uncommonly high for such inhomogeneous systems but they decrease rapidly with the rising temperature; and (iii) it has unique linear magnetoresistance which decreases fast as the temperature rises. A concept is proposed below to explain these anomalies.

It is likely that observed conduction so much different from the impurity conduction of semiconductors is due to the specific transport properties of the object considered that are caused by the carriers emitted by nanocrystallites to silicon. On their way to the Si crystal the carriers have to overcome a surface barrier (induced by the band discontinuity) between the two semiconductors $CrSi_2$ and Si. The electron (hole) escape from nanocrystallites results in charging the nanocrystallites. Note that these charges can build up to many electron charges.

Since the nanocrystallites $CrSi_2$ are within one crystallographic (111) plane of Si, their charges distort the energy spectrum of Si. When the nanocrystallites are charged positively, each of their charge produces hollows (cavities) in the potential plane which is the bottom of the conduction band, and here electrons are accumulated. Similar hollows form also in the ceiling of the valence band. The changes of negatively charged nanocrystallites produce bulges in the ceiling of the valence band where holes concentrate. Similar bulges form also in the bottom of the conduction band. The hollows and the bulges are actually quantum wells for electrons or holes where they occupy the size quantization level. Below we discuss the hollow-version of the electron conduction. In the case of hole the conduction hollow and the conduction band must be replaced with the bulges and the valence band, respectively.

Consider a system in which the bottom of the conduction band contains localized electrons occupying the quantum states in the hollows. In the electric field the electrons can migrate between the hollows using free states in them. The electron transport is carried out either with the help of the tunnel effect or directly through the conduction band, which requires very low activation energy. On the whole, the process resembles the variable-range hopping conduction. However, in contrast to the known variable-type hopping conduction between acceptors and donors in the forbidden band of a semiconductor [5] which is characterized by low mobility, the hopping electron transport discussed here proceeds through the conduction band. This explains the very high carrier mobility at low temperatures. In real space the electrons in quantum wells are localized near the nanocrystallites but they have energies exceeding the Fermi energy.

The investigated object is characterized by very low activation energy in terms of the Arrhenius law. Normally, in silicon containing dissolved impurity atoms (donors or acceptors), but no nanocrystallites, the activation energy would be at least an order of magnitude higher. For example, it is ≈ 0.3 eV in Si with Cr atoms [6]. But such activation transitions could affect the temperature dependence of resistance only at temperatures exceeding those in Fig. 1. In our sample the growth of the carrier concentration with the rising temperature is mainly controlled by the process of electron escape from the nanocrystallites $CrSi_2$. The presence of charges at the nanocrystallites not only produces hollows in the bottom of the conduction band (or bulges in the ceiling of the valence band) and as a result suppresses the activation energy; but it also reduces the distance on the energy scale to the bottom of the conduction band (by electron conduction) or to the ceiling of the valence band (by hole conduction) under the influence of joint charge at the nanocrystallites. We believe that in temperature region II thermally activated holes occupy large bulges produced by large high-charge nanocrystallites. Being saturated at a certain temperature, the process moves to temperature region III where small bulges formed by small nanocrystallites are occupied. The model explains the difference between the activation energies in regions II and III in the Arrhenius law.

Linear positive magnetoresistance is a special case. Here it is considered within a model of interhollow electron hopping through the conduction band. The electron hopping is a random process. The hopping path distribution (Gauss type) is limited by the overlapping length of the wave functions of the states in the quantum wells on the highest-value side and by the smallest nanocrystallite spacing on the low-value side; the average internanocrystallite spacing can be estimated as $a = N^{-1/2}$, where N is the surface nanoparticle density. The parameter L (averaging over the hopping paths) specifies the initial resistance of the system before applying a magnetic field.

When a perpendicular magnetic field is applied, the electron hopping trajectories are bend due to the cyclotron motion. The straight-line distance between the hop start and finish is taken as a mean free path. As the magnetic field grows higher, more and more electrons are involved in hopping to the region next to the hop start and the mean free path decreases. As a result, the addition to the initial resistance increases, i.e. magnetoresistance $\Delta\rho(B)/\rho_0$ grows.

The proposed interpretation of magnetoresistance is based on the relationship between two parameters – the starting average path of the hop L and the cyclotron path length $2\pi r_L$, where $r_L = \hbar k/(eB)$ is the cyclotron radius, $p_F = \hbar k$ is the quasi-momentum. The hopping process in the magnetic field can be described by the function of probability distribution $f = \exp(-L/(2\pi r_L))$ which determines the probability of conservation of the starting characteristics of the system when the magnetic field is applied and specifies the deviation from the initial state (assumed to be equal to unity) when the argument $L/(2\pi r_L)$ increases with the magnetic field. (The function

$f = \exp(-x)$ decreases from 1 at $x=0$ to zero at infinitely growing x.) The deviation indicated by the function

$$F = 1 - \exp\left(-\frac{L}{2\pi r_L}\right) \tag{5}$$

is taken as an addition to resistance due to the magnetic field. The function $F(x)$ increases from zero at $x=0$ to 1 at infinitely growing x. In the region of low x (from $x=0$ to $x \approx 0.5$) the function F is practically linear and described by the $y = 0.8x$ type function. The highest magnetic field used to register magnetoresistance is likely to be within the criterion $L/(2\pi r_L) \leq 1/2$, which is suggested by the estimates below. The quasi-momentum p_F for calculating the cyclotron path can be found using the equation for a two-dimensional system $p_F = \hbar\sqrt{2\pi n}$, where n is the surface electron density. The quasi-momentum is $p_F = 2.5 \times 10^{-21}$ g cm s^{-1} for the highest density $n = 10^{12}$ cm^{-2} at temperature 40 K. In the magnetic field $B=4$ T the cyclotron radius is $r_L \cong 40$ nm. This obeys the above inequality because the equation $L = \pi r_L$ yields quite realistic average path of the hop $L \cong 125$ nm. (The above inequality is strengthened by shorter average hop paths.)

It should be noted that in objects with shorter average hop paths the function equation (5) gives a smaller addition to the initial resistance, which is observed in real situations. For example, when the temperature increases from 25 to 30 K, the mean free path decreases about eight times as is evident from the change in the mobility in Fig. 2b. Correspondingly, the magnetoresistance of the sample (e.g., at $B=3$ T) decreases about six times (Fig. 3). This magnetoresistance–mobility correlation also persists at higher (up to 40 K) temperatures.

The proposed model of electron hopping through conduction band (or hole hopping through valence band) in a two-dimensional conducting system formed by nanocrystallites located within one crystallographic plane of a semiconducting single crystal offers an adequate explanation of the peculiar temperature variation of the resistance in a sample with $CrSi_2$ nanocrystallites in the (111) plane of silicon, the very high carrier mobility at low temperature (20–30 K) and the giant linear magnetoresistance which decreases rapidly as the temperature rises.

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