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Energy Spectrum of Defective Centers in Silicon Doped with Molybdenum

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ABSTRACT

The processes of the formation of defect centers in Si doped with molybdenum have been using the methods of capacitive spectroscopy.

It is shown that the diffusion introduction of molybdenum atoms into silicon leads to the formation of defect centers with deep levels E_C–0.20 eV and E_C–0.29 eV with electron capture cross sections $\sigma_n = 2\cdot10^{-17}$ cm^2 and $\sigma_n = 4\cdot10^{-16}$ cm^2 in n-Si<Mo>. In the p-Si<Mo> samples, one deep level with an ionization energy E_V+0.35 eV and a hole capture cross section $\sigma_p = 7\cdot10^{-15}$ cm^2 was found. It was found that when doped with a molybdenum impurity when growing single-crystal silicon, deep levels are not observed, although According to preliminary data of neutron activation analysis, Mo atoms are present in the bulk of Si in a rather high concentration (~ 10^{16} cm^{-3}).

Key words: Capacitive, diffusion, doping, defect center, deep level, impurity, molybdenum, photocapacity, spectroscopy, silicon.

1.INTRODUCTION

It is known that in recent years the introduction of so-called unconventional impurities - impurities of refractory elements – has been used to modify the electrophysical properties of silicon and control its parameters. These impurities create a number of deep levels in the silicon band gap and have a noticeable effect on the electrophysical parameters of silicon. Specially introduced impurities enter into various interactions with uncontrolled impurities and structural defects of the silicon lattice in the process of technological treatments that accompany almost any route of semiconductor device manufacturing. All these processes determine the formation and development of the defect structure of doped monocrystalline silicon. In this regard, we studied the processes of defect formation in Si, with an impurity of molybdenum Mo, introduced into silicon both by the diffusion method and in the process of growing [1]-[4].

In addition, the introduction of dopants, for example, zirconium, titanium or other refractory elements, into the melt during the growth of large-diameter single crystals contributes to an improvement in the quality of Si: the axial and radial uniformity of the distribution of interstitial oxygen increases, the lifetime of nonequilibrium charge carriers increases [4]-[5].

As shown above, among all unconventional impurities, the behavior of impurities of refractory elements in silicon is the least studied. Moreover, even the available data are scattered and contradictory [4]-[13].

2.;MATERIALS AND METHODS

Therefore, in order to determine the energy spectrum of deep centers created by Mo atoms in Si, we carried out a comprehensive study of the properties of doped samples by deep-level transient spectroscopy(DLTS) and photocapacity methods. The samples under study were initial Si grown by the Czochralski and crucible-free zone melting methods with different resistivities (ρ) in the range 1÷300 Ohm·cm and samples of Si doped with molybdenum when grown from the melt. Diffusion alloying of n-Si and p-Si P with molybdenum impurity was carried out in the temperature range T_{dif} =900÷1200^{0}C for 1÷10 hours from a layer of high purity metal impurities (99.99%) sprayed in vacuum.

The samples were cooled after diffusion of the impurity in different ways. The cooling rate ν_{cool} of the samples after diffusion varied from 0.1^{0}C/s to 40÷80^{0}C/s. As control samples, we used n- and p-type silicon samples heat treated at the same temperature and time as the introduction of Mo into Si. Measurements of the resistivity ρ of silicon samples with refractors elements impurities after diffusion at T_d = 900 ÷ 950^{0}C show that ρ in n-Si and p-Si almost did not change. In n-Si samples at T>1000^{0}C, the values of resistivity ρ after Mo diffusion decreased, and in p-Si the ρ value increased,ρ of the control samples that underwent a similar high heat treatment, almost did not change. From the change in the value of in Si after doping

with molybdenum atoms, it can be concluded that Mo atoms introduce donor centers in Si.

The studies were carried out using non-stationary capacitive spectroscopy of deep levels and photocapacitance.

3.EXPERIMENTAL RESULTS AND DISCUSSION

For capacitive measurements, diodes or Schottky barriers were fabricated from uncompensated crystals by vacuum deposition of gold on n-Si and antimony on p-Si using the technology described in [7]. Ni was chemically deposited or Sb was deposited as an Ohmic contact. The technique for measuring and processing capacitance-voltage characteristics, DLTS spectra, and photocapacitance are described in [14]-[18]. From the capacitance-voltage characteristics, the dependences $1/C^2=f(V_{sample})$, were determined, which were linear in all studied diodes. The concentration of ionized centers in the space charge layer in diodes made of n-Si <Mo>, as well as in p-Si<Mo>, determined from the dependence $1/C^2=f(V_{sample})$ at 300 K, is in good agreement with the concentration of small impurities in the initial Si. Figure 1 shows the dependences $1/C^2=f(V_{sample})$ of a typical n-Si<Mo> at 300 K and 77 K. In all n-Si <Mo> diodes, there is no dark relaxation of the capacitance, i.e. the concentration of levels with E_C<0.15 eV is negligible.

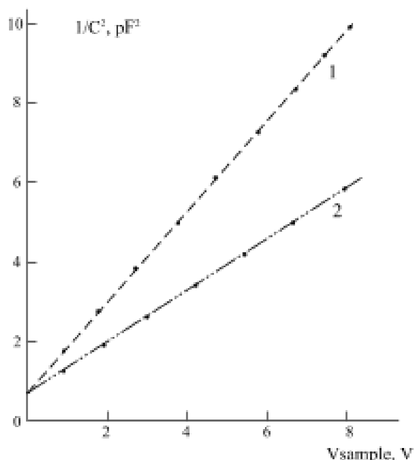

Figure 1: Dependence $1/C^2=f(V_{sample})$ of a typical sample of n-Si <Mo> at 300 K (1) and 77 K (2).

The energy spectrum of the formed deep levels was determined from measurements of the photocapacity and DLTS spectra of silicon samples diffusion-doped with molybdenum, as well as control samples subjected to heat treatment (without impurities).

Figure 2 (curve 1) shows a typical photocapacity spectrum of an n-Si<Mo> -based diode. As can be seen, in the photocapacity spectra of the n-Si<Mo> samples, there is a relaxation of the capacitance near hν~0.20 eV and hν~0.29 eV, associated with the recharge of two deep levels.

To determine the deep levels located in the lower half of the forbidden zone in n-Si<Mo>, the induced photocapacity was measured.

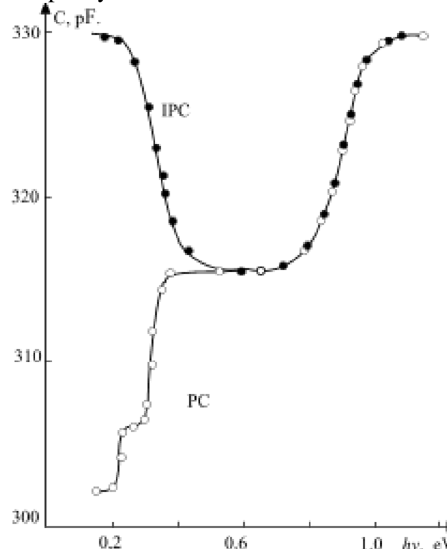

Figure 2: Spectra of photocapacity (curve 1) and induced photocapacity (curve 2), n-Si<Mo> samples doped with molybdenum at 1200°C

For this, the diode was illuminated from the base side for a sufficiently long time with light with hν~1.4 eV. Measurements of the spectra of the induced photocapacity showed that near hν~0.35eV, there is a charge exchange associated with the charge exchange of a level with an ionization energy E_V + 0.35 eV (Fig. 2, curves 1 and 2).

For a more detailed identification of deep defect centers created during the diffusion of molybdenum atoms into silicon, DLTS spectra were measured. Figure 3 shows the DLTS spectra of n-Si and p-Si samples doped with molybdenum at 1200°C followed by rapid cooling.

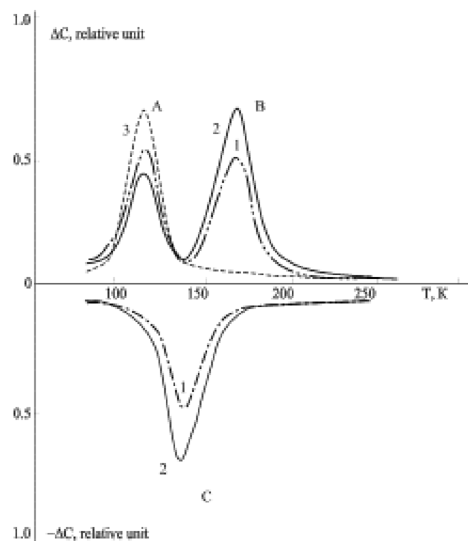

Figure 3: DLTS spectra of n-Si <Mo> and p-Si <Mo>samples,doped with molybdenum at 1000°C and 1200°C(curves 1 and 2) and control heat-treated n-Si samples (curve 3)

Measurements of the DLTS spectra of doped samples (Fig. 3, curves 2 and 3) showed that the spectra of n-Si <Mo> samples exhibit 2 peaks with maxima at temperatures T_{max} = 125 K (peak A) and T_{max}=160 K (peak B), and in p-Si <Mo> there is one peak with a maximum at T_m=190K (peak C).

The recalculation of the DLTS spectra in the Arrhenius dependence and numerical calculations of the parameters of the defects detected upon the introduction of molybdenum atoms into silicon showed that the observed peaks are due to the charge exchange of deep levels with ionization energies E_C–0.20 eV (peak A) and E_C–0.29 eV (peak B) by the cross sections electron capture $\sigma_n=2\cdot10^{-17}$ cm^2 and $\sigma_n= 4\cdot10^{-16}$ cm^2 in n-Si<Mo>. In the p-Si <Mo> samples, one deep level was found with an ionization energy E_V+0.35 eV (peak E) and a hole capture cross section $\sigma_p=7\cdot10^{-15}$ cm^2 (Fig. 3, curve 2).

From a comparison of the photocapacity and DLTS spectra in the doped and control samples, it was found that the E_C-0.20 eV level is also observed in the heat-treated samples (without molybdenum impurity), and its concentration is significantly higher than in the samples doped with molybdenum. Hence, we can conclude that only deep levels with ionization energies E_C-0.29 eV and E_V + 0.35 eV are associated with molybdenum atoms in Si, and the level E_C-0.20 eV is, probably, a defect of heat treatment. Comparison of the photocapacity and DLTS spectra of Si<Mo> samples showed that there is a good correlation between the optical and thermal ionization energies of the levels E_C – 0.20 eV, E_C – 0.29 eV, and E_V +0.35 eV within the measurement error.

We note that deep levels were not observed in the photocapacity and DLTS spectra in silicon samples doped with molybdenum impurity during the growth of single-crystal silicon, although, according to preliminary data from neutron activation analysis, Mo atoms are present in the bulk of Si in a rather high concentration (~ 10^{16} cm^{-3}).

4.CONCLUSION

Comparison of the DLTS results for n-Si <Mo> and p-Si<Mo> samples doped with molybdenum at different temperatures shows that the efficiency of the formation of deep levels associated with molybdenum atoms, as in the case of other refractory elements [19]-[20], depends on the temperature of diffusion T_{diff}. and cooling rate υ_{cool} after it: concentration levels increase with increasing T_{diff}. and υ_{cool}.

Thus, it has been found that the diffusion introduction of Mo into Si leads to the formation of two deep levels in the upper half of the band gap with ionization energies E_C -0.20 eV and E_C - 0.29 eV and one level - in the lower half of the band gap with E_V+0.35 eV. , moreover, only the last two levels are associated with molybdenum atoms, and the E_C-0.20 eV levels, which are also observed in the control heat-treated samples, are, most likely, defects in heat treatment. A detailed analysis of the spectra in Fig. 3 shows that with an increase in the concentration of Mo levels, the concentration of levels of thermal defects sharply decreases. Hence it follows that Mo atoms prevent the formation of thermal defects, that is, they are getters for them.

Analysis and comparison of the data obtained by the methods of capacitive spectroscopy and neutron activation analysis show that not all of the molybdenum introduced by diffusion exhibits electrical activity, only about 20% of Mo atoms in the bulk of Si are electroactive. This behavior of Mo atoms is similar to the behavior of other elements in silicon [3]-[4].

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