Section 4. Physics

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DEEP LEVEL TRANSIENT SPECTROSCOPY OF DEFECTS IN SILICON MULTILAYER STRUCTURES DOPED WITH HAFNIUM ATOMS

Abstract. By means of methods transient capacitance spectroscopy of deep levels has been used to study defect formation in silicon multilayer structures doped with hafnium atoms. It has been established that the presence of electrically active hafnium atoms in the silicon substrate of the MIS structures leads to an increase in the density of the surface states N_{ss} and the appearance of distinct peaks caused by hafnium atoms with deep levels of E_c-0.23 eV and E_c-0.28 eV on n-Si<Hf> and Ev+0.35 eV on p-Si<Hf>. The presence of an electroneutral hafnium impurity in the silicon substrate of the MIS structures does not lead to a change in the density of the surface states of the MIS structures and the DLTS spectra.

Keywords: spectroscopy, silicon, defect, deep level, doping of the impurity, Hafnium, MIS structures.

Introduction

It is known that the doping of silicon with high melting elements significantly affects the performance characteristics of semiconductor devices [1–4]. In addition, there are contradictory data in the literature on the electrical activity of these impurities and their interaction with other defects. In most works there is no information about the electrical activity of these atoms. It is known that high melting elements introduced into silicon from the melt during cultivation, having high chemical activity and a tendency to complexation, are present in silicon in an electrically inactive state.

The processes of doping of semiconductor materials and multilayer structures with acceptor and donor impurities that create shallow levels have been studied quite fully [5], as for doping with impurities of high melting elements, due to the complex nature of the interaction between impurity particles and defects in the semiconductor structure, the influence of heterogeneity of the structure of metal-insulator -semiconductor structures (MIS structures) on redistribution impurities, there is not enough clarity here [6]. It is the presence of such impurities that is associated with the stability of the operating parameters of microchips based on MIS structures.

Experimental part

This work is devoted to the study of the influence of one of the high melting elements – hafnium on the electrophysical properties of silicon multilayer structures of the metal- insulator -semiconductor type (MIS structures) with thermally grown oxide. Silicon doping with hafnium was carried out both by diffusion method and in the process of growing from the melt.

Diffusion doping of silicon with hafnium was carried out in the temperature range 1000 ÷1200 °C for 10 hours from a metal hafnium layer deposited on the Si surface. Then, on plates of n-Si<Hf> with a resistivity of ρ = 10÷40 Ohms cm, a layer of SiO_2 with a thickness of about 800÷850Å at 900 °C was thermally grown in an atmosphere of moist oxygen. By thermal spraying of aluminum on a layer of silicon dioxide, metal electrodes were created, their area was 0.03 cm^2, thickness – 7000 Å.

To study various defects created by Hf atoms and their influence on the properties of the volume and the Si-SiO_2 interface of silicon MIS structures, we conducted comprehensive studies using methods of deep level transient spectroscopy spectroscopy in the constant capacitance mode (CC-DLTS) and high-frequency volt-farad characteristics (C–V characteristics). The concentration of possible deep levels in the silicon volume was measured by the C-DLTS method on Schottky barriers made on silicon after the SiO_2 layer was etched [7–8].

Results and its discussion

From measurements of the volt-farad characteristics of MIS structures based on silicon diffusionally doped with hafnium, it was found that they are shifted towards negative displacements compared to the control MIS structures. This indicates that the diffusive introduction of hafnium into silicon leads to an increase in the density of the surface states of the MIS structures and the formation of a positive charge at the Si-SiO_2 interface.

Measurements of CC-DLTS spectra in Si-based structures doped with hafnium in the process of growing from the melt and control MIS structures (without hafnium impurity) showed that their spectra practically coincide and there is no noticeable concentration of any deep levels, although according to neutron activation analysis, the content of hafnium atoms is quite high, of the order of $2\times10^{16}\div5\times10^{18}$ cm^{-3}. This indicates that after doping silicon with hafnium during the growing process, no deep levels are formed in the forbidden zone of the silicon substrate. Consequently, the hafnium atoms introduced during the growing process are in the silicon volume in electron-neutral states.

Studies have shown that they can be activated using high-temperature treatments. At the same time, the energy spectrum of deep levels is similar to samples doped with hafnium by diffusion method (Fig. 1, curve 2). Note that the concentrations of deep levels bound to Hf atoms in Si<Hf> $_{diffusion}$ samples (Fig.1, curves 3 and 4) are an order of magnitude higher than in Si<Hf>$_{growing}$ samples.

Analysis and measurement of CC-DLTS spectra of MIS structures based on silicon diffusionally doped with hafnium (Fig. 1, curves 3 and 4) and control MIS structures (Fig. 1, Curve 1) showed that 2 peaks with maxima at temperatures T_{max} = = 110 K and T_{max} = 146 K, and no such peaks were found in the control samples. Numerical calculations of the parameters of defects caused by these peaks showed that the peak with a maximum at T = 110 K corresponds to the level with an ionization energy of E_c – 0.23 eV, and the peak at T = 146 K corresponds to the level with an ionization energy of E_c – 0.28 eV.

Measurements of the density distribution of N_{ss} surface states over the band gap width of the semiconductor units of silicon MD structures with and without hafnium impurity have shown that the distribution spectrum of the dependence of N_{ss} on E_g has a typical U-shaped character. Analysis of these dependencies showed that the presence of hafnium in the substrate does not lead to noticeable changes in the distribution of N_{ss} over E_g and the formation of any pronounced peaks.

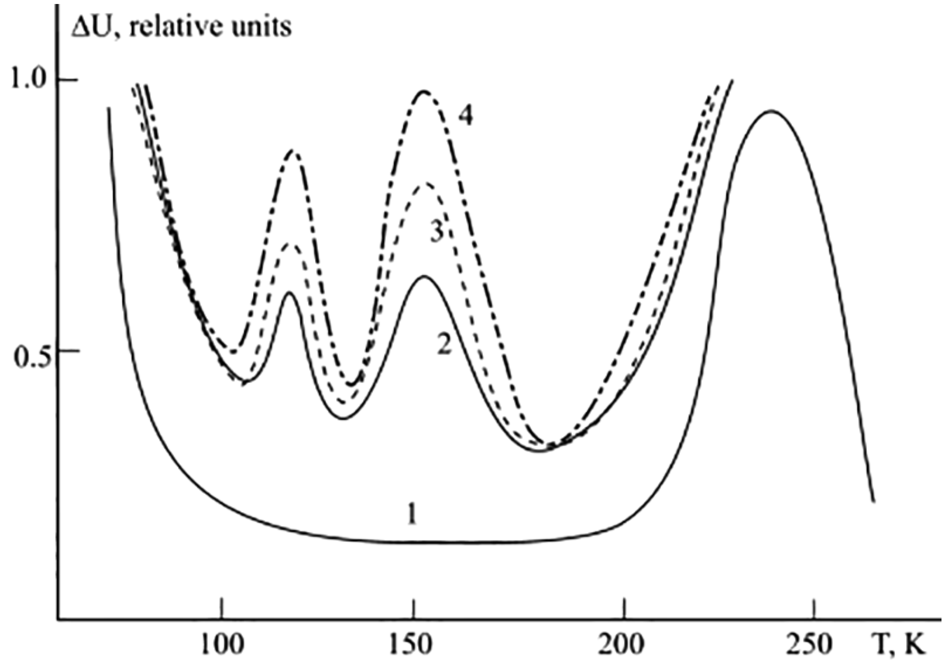

Figure 1. CC-DLTS spectra in MIS structures with Hf introduced at growing (curve 1), at growing+ heat treatment (curve 2) and introduced by diffusion (curves 3, 4)

It is established that the presence of electrically active hafnium atoms in the substrate of multilayer structures of the Al-SiO_2-n-Si<Hf> type leads to noticeable changes in the CC-DLTS spectra and two pronounced peaks in the energy range with values of E_c – 0.23 eV and E_c – 0.28 eV are observed on the spectra in doped structures. To identify these defects with certain impurities, SiO_2 layer was removed in the studied MIS structures and Schottky barriers were made on them. Gold was sprayed onto the n-Si<Hf> substrate as a Schottky barrier, and antimony was sprayed in high vacuum as an ohmic contact.

Typical DLTS spectra of the n-Si<Hf> and p-Si<Hf> samples measured at the obtained barriers were similar to the spectra in Fig.1. Processing of the DLTS spectra and their analysis show that in the n-Si<Hf> samples, two deep levels with ionization energies E_c – 0.23 eV and E_c – 0.28 eV. In the samples of p-Si<Hf>, one deep level with an ionization energy of E_v+0.35 eV was detected. Analysis of the DLTS spectra showed that the levels with the ionization energy E_c – 0.28 eV and E_v+0.35 eV are associated with hafnium atoms in Si. These results confirm the data obtained from measurements of CC-DLTS spectra.

Conclusion

Thus, the analysis of the obtained results shows that the parameters of deep levels in MIS structure do not differ from the parameters of the corresponding levels observed in Si diffusionally doped with hafnium.

It has been established that the presence of electrically active hafnium atoms in the silicon substrate of the MIS structures leads to an increase in N_{ss} and the appearance of distinct peaks associated with hafnium atoms, and the presence of an electroneutral hafnium impurity in the silicon substrate of the MIS structures does not lead to a change in the density of the surface states of the MIS structures and the DLTS spectra.

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