Technology for the formation of refractory metals for micro- and nanoelectronics products

G A Mustafaev¹, A I Khasanov²,³, N V Cherkesova¹ and A G Mustafaev⁴

¹ Kabardino-Balkarian State University, 173, Chernyshevsky St., Nalchik, Russia
² Chechen State University, 17a6 Dudayev Boulevard, Grozny, 364060, Russia
³ Kh. Ibragimov Complex Institute of the Russian Academy of Sciences, 21A, Staropromyslovsky ave., Grozny, Russia
⁴ Dagestan State University of National Economy, building 43-a, Gadzhiev Str., Makhachkala, Russia

E-mail: zoone@mail.ru, aslan2001@rambler.ru, natasha07_2002@mail.ru, arslan.mustafaev@mail.ru

Abstract. Metal silicides play a significant role in the preparation of ohmic contacts and Schottky barriers on silicon. The formation of ohmic contacts is carried out by applying a metal film with a thickness of ~ 100 nm to silicon, followed by annealing at temperatures of 400–600 °C, as a result of which there is a reaction between silicon and metal with the formation of silicide. With this technology, silicon diffusion leads to instability of devices. In this regard, the authors developed an improved technology for the formation of silicides of refractory metals to obtain ohmic contacts. Ion implantation allows, due to ionic mixing, forming nickel silicide on the surface of the samples when heated. It is important that, with an increase in the radiation dose, the formation of Ni₂Si silicide slows down. This effect can be explained by the formation of a dielectric Ni₃Si₂. Similar phenomena were observed during the bombardment by oxygen and nitrogen ions.

1. Introduction

One of the methods for the production of silicides is the deposition of thin films of platinum and silicon, and the synthesis of alloys. The dissociation of SiH₄ molecules into elemental silicon and various molecular fragments leads to the deposition of silicon on the discharge electrode and its surrounding surfaces. The degree of dissociation depends on the output power of glow discharge. In the process of reactive sputtering, in which reactive gas dissociates into solid products, the stoichiometry of the films depends on the deposition rate of the target material and the substrate, re-sputtering from the target and the speed of sputtering of target material [1–2].

Thus, at low powers and high partial pressures of the reactive gas, the dissociation rate will be sufficiently high, so that the target is completely covered by the sputtering product. At high powers and low partial pressures, the sputtering rate of the target material exceeds the dissociation rate of the reactive gas, which leads to sputtering of the target material. The necessary stoichiometry of the deposited substance is obtained by selecting the atomization power and pressure of the reactive gas. Figure 1 shows the change in the Si/Pt concentration ratio in the film as a function of the SiH₄ flow rate for cathode voltages of 700 and 900 V.
Figure 1. Ratio of Si / Pt concentrations in the film depending on the SiH₄ flow rate for cathode voltages of 700 and 900 V

As it can be seen from Figure 1, at low powers, the Si/Pt ratio is very small at the beginning and rapidly increases at flow rates above 1.7. At flow rates greater than 2.2, platinum was not detected in the films. At high powers, the change in the Pt/Si ratio depending on the silane flux occurs more smoothly. This indicates that more precise control over stoichiometry can be carried out at high atomization powers.

Figure 2. Dependence of resistivity on silicon concentration for films deposited at 20 °C and 900 V at the cathode

The change in resistivity as a function of silicon concentration for films deposited at room temperature and a voltage of 900 V at the cathode is shown in Figure 2. The specific resistance of the
platinum film is ~ 22 μm cm and increases linearly with increasing silicon content up to 65 %. Above 65 %, a sharp increase in resistance is observed, which indicates semiconductor conductivity. This result is consistent with x-ray diffraction and electron microscopy.

Silicides of refractory metals also attract attention as a material for metallization of IC [3, 4]. Metal disilicides Ti, Nb, Ta, Mo, W are low-resistant, their potential use is as gate electrodes in VLSI. Replacing polycrystalline Si in gate metallization with low-resistance refractory metal silicides can get around the limitations inherent in high-resistance doped polysilicon. Refractory silicide films deposited on polysilicon act as shunt layers for polysilicon gate electrodes. In order to simplify metallization schemes, these multilayer structures can be replaced by silicide films.

Refractory metal silicides are prepared on silicon substrates from metal halides, reduced by H\textsubscript{2} or Si to form refractory metals (for example, Mo, V or Ti); then the metal is converted into metal disilicide by diffusion of atoms at sufficiently high temperatures (in this case, it is necessary to exclude the reduction of the metal halide with silicon in order to limit the erosion of the silicon substrate).

Silicon refractory metals can also be obtained by direct diffusion of atoms from a silicon layer chemically deposited from the vapor phase into a substrate of refractory metal, such as Mo, at temperatures of 1000–1200 °C. The high temperatures necessary for the recovery of metal halides and interdiffusion of elements lead to mechanical stresses and the formation of voids at the interface between the silicide and the substrate. In addition, the above processes for the preparation of metal silicides can be used only on substrates made of silicon or refractory metal.

In the self-aligned MOS technology for the formation of refractory metal silicide films in the source and drain regions, metal films are deposited by physical methods (with subsequent interdiffusion of the metal and silicon at high temperatures). An alternative method involves the direct deposition of refractory metal silicide films based on the reaction of a silicon-containing gas (silane, chlorosilane, silicon tetrachloride) with a gaseous metal compound. In order to control the composition of films grown by chemical vapor deposition, the thermal stability of the gaseous metal compound and the silicon-containing molecules must be sufficiently high.

2. Experiment
Refractory silicides are most compatible with conventional MOS technology, and the most suitable for interconnects and contacts are the metal disilicides Mo, Ta, Ti and W. These conductive materials, chemically deposited from the vapor phase, have the necessary properties for their use in gate electrodes.

Titanium silicide films were chemically deposited on a silicon substrate from gas mixtures of TiCl\textsubscript{4}-SiH\textsubscript{4} or TiCl\textsubscript{4}-SiH\textsubscript{4}-Ar at temperatures of 600–850 °C. The specific resistance of these films is very close to the volume value of 10 μm*cm. Chemical deposition of TiSi\textsubscript{x} films (x = 1) from the vapor phase in the plasma was carried out at 450 °C in a system with a hot wall. Polysilicon structures were grown on doped layers from an amorphous silicon layer 100 nm thick, TiSi, 1 120 nm thick, and an amorphous silicon layer 15 nm thick. Processing in plasma helped to clean the interface between the substrate and the film. In these multilayer structures, the lower layer of amorphous silicon serves as a source of excess silicon during subsequent heat treatment, and the upper layer of amorphous silicon protects amorphous titanium silicide from oxidation. Thermal annealing of these structures at 650 °C leads to the formation of TiSi\textsubscript{2} layers with a specific resistance of 14 μm*cm. Such a process can be used to form a polycide (polysilicon silicide) gate electrode of titanium silicide deposited on polysilicon in the same cycle in which polysilicon was doped.

In order to precipitate tungsten silicide from WF\textsubscript{6}-SiH\textsubscript{4} mixtures in a low-pressure reactor with a cold wall, reactive gases are introduced into the reactor by separate injection and mixed near the surface of the substrate to minimize bulk reactions resulting in a powdery material. Tungsten silicide films were prepared from a gas mixture of SiH\textsubscript{4}-WF\textsubscript{6}-He at temperatures of 350–450 °C and a pressure of 7–40 Pa. The growth rate varied from 50 to 100 nm/min and does not depend on the substrate temperature, pressure, and SiH\textsubscript{4} flow rate.
The composition of the film is determined by the ratio of the flow rates of SiH$_4$-WF$_6$. They are enriched in silicon (composed of a mixture of Si + WSi$_2$), and become polycrystalline after annealing at a temperature of 900–1000 °C. The specific resistance is 40–50 μm*cm. The surface resistance of a Si-enriched tungsten silicide film with thickness of 250 nm chemically deposited directly into a gate oxide 65 nm thick is 1–4 Ohm/m, depending on the temperature and annealing time.

With the transition of MMSII technology of devices to the submicron range of element sizes, in order to increase the speed and functional density, the value of the series resistance of the structures increases.

In this regard, it is necessary to use self-aligned silicide contacts, which reduce the resistance of the gate, n$^+$ and p$^+$-regions of the source and drain by 1–2 orders of magnitude. It is necessary to take into account that the formation of such contacts is not just an additional operation to the proven technology; in this process, during the formation of the silicide, a certain layer of silicon is absorbed, together with the doping impurity contained in it – the thickness of the absorbed Si layer is 1.5 times greater than the layer deposited participating in the Ti reaction. As a result, it is possible to reduce the impurity concentration near the TiSi$_2$/Si interface and, as a result, the unacceptable resistance of the contact layer. At the same time, if the silicide layer extends to the depletion region near the edge of the oxide insulation, transition leaks may occur.

The formation of TiSi$_2$/Si contacts on n$^+$ and p$^+$ material was studied for various values of the Ti layer thickness in shallow areas of the source and drain. The effective contact resistance between the n$^+$ region and the silicide layer is determined by two equipotential surfaces; it is due to the finite value of the specific resistance at the TiSi$_2$/Si interface and it also includes the Si resistance under silicide.

Figure 3 shows the dependence of the contact resistance in the MOS structure on the diffusion depth of As in Si for different thicknesses of the Ti layer.

![Figure 3. Dependence of contact resistance in the MOS structure on the depth of diffusion of As into silicon for different Ti layer thicknesses](image)

The dependence of the contact resistance in the MOS structure on the diffusion depth of As in Si for different Ti layer thicknesses characterizes the contribution of the contact resistance to the series resistance of the device; both curves were determined for equal doses of As implantation (2\times10^{15} \text{ cm}^{-2}), followed by heat treatment at 900–950 °C for 30–60 min to obtain different transition depths. With a Ti layer thickness of 50 nm, the resistance of the TiSi$_2$ layer is 4 Ohm/m, and with a transition depth of more than 0.30 μm, a low contact resistance is achieved. For a transition depth of 0.15 μm, the contact resistance is significantly higher.
The increase in the contact resistance with a decrease in the depth of the source and drain regions is reasoned by the relatively large thickness of the Si surface layer absorbed during the formation of TiSi2 (i.e., a decrease in the final thickness of these regions) and can cause significant degradation of the current – voltage characteristics and dynamic conductivity at a low channel resistance (especially the submicron channel lengths), in the case of low voltage at the drain and high voltage at the gate.

At a Ti layer thickness of 50 nm, the As concentration near the TiSi2 / Si interface is only 3 × 10^{19} cm\(^{-3}\). The contact resistance can be decreased reducing the thickness of the Ti layer to 35 nm, then the As concentration near the interface will exceed 10^{20} cm\(^{-3}\). At a diffusion depth As of 0.15 \(\mu\)m and a Ti layer thickness of 35 nm, a silicide layer resistance of 6 Ohm/m and a pair of contacts of no more than 300 Ohm*\(\mu\)m were obtained. This is quite satisfactory when compared to a minimum channel resistance of 2000 Ohm*\(\mu\)m in the linear region for a MOS FT with an n-channel with the length of 0.3 \(\mu\)m.

The resistivity of the contacts on the n\(^+\) – layers is about 3 times lower than on the p\(^+\) – layers; this may be due to the difference in the effective mass of the electron and the hole, since the work function for TiSi2 corresponds to the same barrier height on n and p type Si layers.

Molybdenum is most acceptable in terms of adhesion to the silicon dioxide layer. In the case of thermal burning of Mo into Si, the natural oxide on the Si surface causes the process carried out at elevated temperature and impairs the reproducibility of the silicide formation, and strong stresses arise around the periphery of such contacts. In order to lower the temperature of silicide formation, interstitial ions of various elements were used, which caused Mo to be mixed with Si.

The use of inert gas ions for mixing leads to the formation of bubbles in the contact area that impair the reliability of the contacts. If mixing is performed using B, P or As, then simultaneously with the formation of the silicide, substrate doping is achieved. Mo/Si contacts were formed for the samples created by ion implantation of phosphorus ions P\(^+\).

The studies were performed on Si p-type plates (4.5 Ohm*cm) with an orientation of (100). Mo deposition with a thickness of 100 nm was carried out at a substrate temperature of 3000 \(^{\circ}\)C using a magnetron source. Ion introduction of phosphorus P with a dose of 10^{16}–10^{17} cm\(^{-2}\) was performed at a substrate temperature of 25, 150 and 300 \(^{\circ}\)C, energy of 250 keV. X-ray diffraction analysis showed that at a dose of phosphorus ions P up to 10^{16}–10^{17} cm\(^{-2}\), reproducibly ensures the formation of the MoSi2 phase. At a dose of 1016 cm\(^{-2}\), Mo is not completely absorbed during the formation of the silicide, and unreacted Mo remains on top of the MoSi2 layer; at a dose of 10^{17} cm\(^{-2}\), all Mo is spent on the formation of silicide.

The measured values of the contact resistance for different conditions of the ionic introduction of phosphorus ions P made by the four-probe method [5] on the samples showed that the contacts have a resistance of ~ 8 Ohms. These results confirm the possibility of reproducible formation of low-resistance contacts at doses of 10^{16}–10^{17} cm\(^{-2}\).

After ion-doping, high-temperature annealing was performed to electrically activate impurity atoms and recrystallize the damaged Si surface layer. In the work, the samples that underwent ionic introduction of phosphorus P ions at a temperature of 25 \(^{\circ}\)C were additionally annealed at 1000 \(^{\circ}\)C in a H2 hydrogen atmosphere for 30 min. At doping doses of 10^{16}–10^{17} cm\(^{-2}\), the contact resistance changed insignificantly. Annealing at 850 \(^{\circ}\)C (also 30 min in a hydrogen H2 atmosphere) for a sample with a dose of 10^{17} cm\(^{-2}\) did not cause the surface roughness of the silicide layer to appear, whereas without ionic introduction of phosphorus, the surface became rough.

Atomic mixing by the action of an ion beam of phosphorus with large doses creates the possibility of the formation of MoSi2 at a significantly lower temperature. The ion beam causes cascade mixing in the surface layer of the sample and diffusion accelerated by irradiation; in the first process, atoms are mixed during collisions, and in the second, diffusion is accelerated as a result of the increase in the density of vacancies and the concentration of interstitial atoms. Since the main effect of increasing the dose of ionic implantation P and the temperature of the sample during this treatment is the increase in grain size, accelerated diffusion can be considered as the main process, which can lead to migration of grain boundaries.
In the research, ion bombardment was also used to improve the uniformity of the properties of Ni2Si films. Nickel silicide films were formed on Si wafers, the surface of which was previously subjected to cleaning by various methods [6].

Immediately after cleaning, the plates were placed in a spraying unit. Ni films 30–50 nm thick were deposited in a vacuum of $10^{-5}–10^{-6}$ Pa at a rate of 2 nm/s. Then the samples were irradiated with xenon ions with energy of 300 keV at room temperature or at a temperature of 170 °C. The radiation doses were $5–10^{13}$, $10^{14}$, $5–10^{14}$ and $10^{15}$ cm$^{-2}$.

Next, the samples were placed in a vacuum oven to form nickel silicide. Ni films were annealed for 20 min at a temperature of 250 °C. An identical procedure was carried out for the case of 180 keV arsenic ion bombardments.

A study of backscattering spectra showed that immediately after xenon ion bombardment, the effect caused by it is noticeable only for a dose of $10^{15}$ cm$^{-2}$. At lower doses, the backscattering spectra corresponded to unirradiated samples. In contrast, after annealing, the effect was noticeable in the samples irradiated with small doses. After annealing the irradiated sample, a Ni2Si layer is present in it, which is more uniform than in the sample subjected only to heat treatment.

3. Conclusion

The experiment showed that the formation of a Ni$_2$Si layer also occurs when arsenic ions are used for implantation, and then the samples are subjected to heat treatment.

Ion implantation allows (due to ionic mixing) forming nickel silicide on the surface of the samples under heating, regardless of the type of previous surface cleaning [7, 8]. It is significant that, with the increase in the irradiation dose, the formation of Ni$_2$Si silicide slows down. This effect can be explained by the formation of a dielectric Ni$_3$Si$_2$. Similar phenomena were observed during the bombardment by oxygen and nitrogen ions.

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