Phase Interactions in TiN$_x$(TiB$_x$)–$n$-Si–$n^+$-Si Contacts and Their Thermal Degradation Due to Rapid Thermal Annealing

N. S. Boltovets*, V. N. Ivanov*, R. V. Konakova**, V. V. Milenin**, and D. I. Voitsikovskii**

* Orion Research Institute State Enterprise, ul. Ê. Pot’ë 8a, Kiev, 03057 Ukraine
** Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, pr. Nauki 45, Kiev, 03028 Ukraine

E-mail: konakova@isp.kiev.ua

Received September 9, 2002

Abstract—The temperature stability of TiN$_x$(TiB$_x$)–$n$-Si–$n^+$-Si, Au–TiN$_x$(TiB$_x$)–$n$-Si–$n^+$-Si, and Au–Ti(Mo)–TiN$_x$(TiB$_x$)–$n$-Si–$n^+$-Si Schottky-barrier contacts subjected to rapid thermal annealing in hydrogen at temperatures $T = 400, 600$, and $800 \degree$C is studied. It is shown that structural and morphological transformations and the related degradation of electrophysical characteristics in interstitial alloys (titanium nitrides and borides) start at $600 \degree$C. Reasons for the degradation of the barrier properties of titanium borides and nitrides are discussed. © 2003 MAIK “Nauka/Interperiodica”.

INTRODUCTION

In recent years, increasingly stringent requirements for the stability of metal–semiconductor contacts in solid-state electronic devices have stimulated the search for novel metallization materials that provide the stability of contact parameters under severe environmental conditions. Among the promising contact materials are nitrides, carbides, and borides of transition metals (from Groups III–VI). These compounds offer metallic properties and also are chemically inert and temperature resistant. Titanium nitride ranks first in this list, as indicated by the number of publications.

Titanium nitride films are already being used as ohmic and barrier contacts in electronics [1]. It seems, however, that their usage as barriers preventing diffusion in multilayer thin-film metallization systems of semiconductor devices will be even more promising. Data for contacts using boride-based interstitial alloys are scarce, although available information indicates that interdiffusion, including reactive diffusion, at interfaces is suppressed when they are employed in metallization systems [2, 3].

The application of interstitial alloys is limited because detailed knowledge of the mechanisms behind the degradation and failure of contacts using these alloys is lacking. Of great importance in this respect is to understand the nature and properties of the transition layer (especially its diffusion-preventing capability).

In this work, we study the temperature stability of Ti-based interstitial alloy layers applied on Si alone and in combination with other metal layers.

EXPERIMENTAL

The samples used were standard silicon $n$–$n^+$ structures prepared by vapor-phase epitaxy. The thickness of the $n$ layer and the donor concentration in it were, respectively, 1–2 $\mu$m and $(8–9) \times 10^{16}$ cm$^{-2}$. For the $n^+$ substrate, these values were, respectively, 300 $\mu$m and $(2–3) \times 10^{19}$ cm$^{-3}$. TiB$_x$ layers were applied on the chemically cleaned surface of the epitaxial layer by the magnetron sputtering of titanium boride. TiN$_x$ layers were applied both by the magnetron sputtering of compact stoichiometric TiN targets and by thermoreactive ion synthesis. The contact layers of titanium, molybdenum, and gold were applied by electron-beam evaporation at a pressure of $=6.6 \times 10^{-4}$ Pa. The thicknesses of these layers did not exceed 100 nm. Rapid thermal annealing (RTA) of the contacts was carried out at 400, 600, and $800 \degree$C in the hydrogen atmosphere for 60 s.

The mechanisms of contact formation and the temperature stability of the contacts were studied by SEM, AES, XPS, and microprobe analysis, as well as by taking static $I$–$V$ characteristics. The structure and morphology of the contacts, as well as the component distributions in them, were investigated using $10 \times 10$-mm metallized test systems formed on $n$-Si–$n^+$-Si substrates. The $I$–$V$ characteristics were taken from Schottky-barrier diodes with a diameter of 100 $\mu$m that were made by photolithography in the form of mesas.

RESULTS AND DISCUSSION

(i) TiN$_x$-based contacts. Consider first a simple TiN$_x$/Si system. Factors influencing the barrier properties of such contacts were revealed by studying the...
structure, chemical composition, and morphology of the TiN<sub>x</sub> films before and after temperature actions.

Figure 1 shows electron diffraction patterns from TiN<sub>x</sub> films obtained by thermoreactive ion synthesis. The diffuse diffraction lines indicate their quasi-amorphous state. This result was supported by X-ray diffraction studies. From X-ray diffraction data for the TiN<sub>x</sub> films, we calculated the fractions of the amorphous and polycrystalline phases in the films, grain size L, lattice spacing a, and macrostresses σ (see Table 1).

As follows from Table 1, as the RTA temperature increases, the quasi-amorphous TiN<sub>x</sub> layer recrystallizes into polycrystalline with a grain size of ≈40 nm. Simultaneously, residual compression stresses in the TiN<sub>x</sub> film are reduced, the reduction being the stronger, the thinner the film.

Along with this change in the mechanical stresses in the heterosystem, the recrystallization of the TiN<sub>x</sub> films should also have an effect on the parameters of the transition layer, i.e., on the barrier properties of the TiN<sub>x</sub> film. This supposition was supported by AES depth profiles in the film (Fig. 2). These results show that the extent of the interface (transition layer) noticeably changes at 600°C (i.e., under RTA conditions), when intense transformations of the structure and morphology of the TiN<sub>x</sub> film are observed. The intriguing fact is that the expansion of the transition layer does not follow the simple exchange mechanism of interface formation. Since titanium nitrides are chemically inert [6] and the oxygen present in the film seems to be in the bound state, producing titanium oxides and titanium oxynitride, the properties of the TiN<sub>x</sub>/Si interface should be governed by competitive Ti–Si and N–Si reactions and depend on the number of free or dissociated Si, Ti, and N atoms and on the permeability of the TiN<sub>x</sub> film. Note that the latter reaction is a high-temperature process because of the high energy of N diffusion activation in Si (=3.7 eV) [7].

Thus, the interface of the contact is nonuniform. As the RTA temperature grows, the structural-phase nonuniformity of the transition layer may increase because of both the recrystallization and diffusion mobility, which causes mixing in the TiN<sub>x</sub>/Si system and chemical reactions between the components of the contact pair. However, in view of the low permeability of the TiN<sub>x</sub> film and an insufficient amount of free Si atoms, one may expect that the interface in the heteropair will remain sharp up to high annealing temperatures, just as follows from Fig. 2.

It should be noted that the above scenario of chemical and structural transformations of the interface ignores the formation of a thin oxide layer on the surface of the semiconductor. The presence of SiO<sub>2</sub> may appreciably suppress chemical processes in the transition layer and, thereby, improve the temperature stability of the contact.

Actually, contacts comprise several films of different metals in order to satisfy many requirements for a contact structure. When combining with one another and also with TiN<sub>x</sub> through mutual boundaries, these metals may significantly affect the TiN<sub>x</sub> barrier properties and, accordingly, the electrophysical parameters of the contacts.

The basic multilayer structures used in this work were Au/TiN<sub>x</sub>/Si, Au/Ti/TiN<sub>x</sub>/Si, and Au/Mo/TiN<sub>x</sub>/Si. It turned out that the degradation mechanism for all three structures is the same. The only difference is that the Mo layer serves as an additional diffusion barrier, because the mutual solubility of Mo and Au is low [8].

Let us consider the thermal degradation of multilayer contact structures in detail with Au/Ti/TiN<sub>x</sub>/Si.

Figure 3 shows the morphology of the layered contact subjected to RTA. Table 2 demonstrates the variation of the atomic structure at different metallization sites (sites 1–4) according to the microprobe analysis data.