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Ohmic Contacts for High Power and High Temperature Microelectronics

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1. Introduction

The increased requirements to the microelectronics regarding the device potential for work at high temperatures, high powers, and high frequencies and in harsh environments engendered the increased interest to the wide band-gap semiconductors. They are considered as a third generation materials in the semiconductor industry, after Si and Ge, and A³B⁵ compounds and their solid solutions. Several materials of the wide band-gap semiconductor group such as SiC, III-V nitrides (GaN, AlN, c-BN), ZnSe, and diamond are very important for the device industry. The unique combination of physical properties in these materials allows development of devices, which could be applied in fields where the devices of the first and second generations cannot be used. Whereas Si and GaAs are chemically stable at 400 °C and 650 °C, respectively, SiC and III-V nitrides are stable up to 1000 °C (Meyer & Metzger, 1996). This high thermal stability allows development of new class high temperature and high power devices with maximal working temperature of 600 °C, which is three and four times higher than this one of GaAs and Si devices, respectively.

Among the wide band-gap semiconductors, SiC and GaN have been most successfully applied in the device fabrication. These semiconductors offer a higher electric breakdown field (4-20 times), a higher thermal conductivity (3-13 times), and a larger saturated electron drift velocity (2-2.5 times) in comparison with silicon. These features make them very useful materials in development of high temperature and high power devices. The advantages of SiC and III-V nitrides technologies allowed manufacture of SiC-based and GaN-based devices such as unipolar high-voltage power FETs (MOSFET, JFET and HEMT), bipolar power diodes (p-n and p-i-n) and transistors (BJT, IGBT and HBT).

The existing applications present many challenges in obtaining high-performance ohmic contacts because they are limiting for device functioning. The ohmic contacts are a critical factor that could restrict the high power and high temperature device application. The high operating temperatures may cause diffusion processes in the contact layer and reactions between the contact components, which could lead to changes of the contact properties during operation at high temperatures, and deterioration of the devices. If the contact resistivity is not sufficiently low inadmissible high voltage drop could arise due to the high current density in the contact of the high power devices. Hence, the following requirements to the ohmic contacts are decisive for application in high power and high temperature microelectronics:

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- *Low contact resistivity* in general, the make of low resistivity ohmic contacts is difficult for wide band-gap semiconductors due to the difficulty in doping and, in the case of p-type materials, due to the wide forbidden band-gap.
- *High temperature stability* this problem is very important in the wide band-gap semiconductors. In the Si and GaAs devices the maximal working temperature is limited by the material stability, because of that the problem of the contact stability is important but not critical. The great potential of SiC and III-V nitrides regarding the capacity for a work at temperatures up to 600 °C and higher, set strong requirements to the thermal stability and reliability of the contacts.
- *Reproducibility* this requirement is important in the case of the device production. Therefore the contact technology should allow the achievement not only good performance, but good reproducibility.

The listed requirements point that the operation of high temperature and high power SiC and GaN-based devices under severe conditions demands development of electrically, thermally and chemically stable metal contacts.

2. Theoretical base of the ohmic contacts

The metal-semiconductor contact is one of the main elements of the semiconductor device structure, which parameters may significantly affect the device working characteristics.

When the metal comes into a contact with the semiconductor, a potential barrier is formed at the interface. Usually, this barrier has rectifying properties and it is named "Schottky barrier". Two types of metal-semiconductor contacts are known: ohmic and Schottky contacts. The Schottky contacts are metal-semiconductor contacts in which a Schottky barrier is formed. The ohmic contacts are metal-semiconductor contacts, which have linear and symmetrical I-V characteristic and a negligible contact resistance as compared to the bulk or series resistance of the semiconductor. They realize the connection between the chip and package in the semiconductor devices.

The presence of ohmic properties is determined by the shape and slope of the I-V characteristic. The main parameter characterized the ohmic contact is the resistivity (specific resistance), which is defined as (Yu, 1970; Sze, 1981)

$$\rho_{c} \equiv \left(\frac{\partial J}{\partial V}\right)_{V=0}^{-1}$$
(1)

According to the definition, the theoretical expressions for contact resistivity could be determined from the I-V characteristics taking into account the current transport mechanism through the contact (Yu, 1970). Four basic mechanisms are considered determinative for the current transport in the metal n-type semiconductor contact when a forward voltage is applied: 1) Emission of electrons from the semiconductor into the metal over the top of the barrier (thermionic emission). 2) Quantum-mechanical tunnelling through the barrier (field emission). 3) Recombination in the space-charge region. 4) Hole injection from the metal into the semiconductor. Depending on the carrier concentration the current transport through the contact is realized mainly by thermionic emission (TE) or field emission (FE). At a low semiconductor doping level ($N_D < 10^{17}$ cm⁻³ ≤ ND ≤ 1020 cm⁻³) the depletion layer width decreases; the barrier becomes thinner and a part of electrons tunnel through it. With highly

doped semiconductors (ND>1020 cm-3) and low temperatures the current transport is determined by the field emission through the barrier only. These processes are defined by a characteristic energy E00 (Padovani & Stratton, 1966):

$$E_{oo} = \frac{q\hbar}{2} \sqrt{\frac{N_D}{m_n \varepsilon_s}} , \qquad (2)$$

where \hbar is a Plank's constant h divided by 2π ; m_n^* is an effective electron mass in the semiconductor. The factor kT/E_{00} (where k is a Boltzmann's constant, and T is the absolute temperature) is a criterion for the interrelation between thermionic and field emission processes. The characteristic energy E_{00} correlates with the tunnelling probability and increases with the semiconductor doping level due to the decrease of the depletion layer width. The thermionic emission occurs at $kT/E_{00}>>1$. When $kT/E_{00}\cong1$ these two processes are comparable and the current transport mechanism is named thermionic-field emission. The field emission is predominating at $kT/E_{00} << 1$.

With thermionic emission the contact resistivity depends on the potential barrier height only (Yu, 1970):

$$\rho_c = \frac{k}{q A^* T} \exp\left(\frac{q \varphi_{Bn}}{kT}\right). \tag{3}$$

In this case, metals formed a potential barrier with low height should be chosen to obtain contacts with low resistivity. With moderately doped semiconductors (thermionic-field emission), the resistivity is determined by both, the barrier height and the doping level of the semiconductor:

$$\rho_{c} = \left[\frac{k}{qA^{*}T}\right] \frac{kT}{\sqrt{\pi(\varphi_{Bn} + V_{n})E_{oo}}} \cosh\left(\frac{E_{oo}}{kT}\right) \left[\sqrt{\coth\left(\frac{E_{oo}}{kT}\right)}\right] \exp\left[\frac{\varphi_{Bn} + V_{n}}{E_{o}} - \frac{V_{n}}{kT}\right], \quad (4)$$

where E_0 is a measure of the probability for tunnelling through the potential barrier and

$$E_o = E_{oo} \operatorname{coth}\left(\frac{E_{oo}}{kT}\right).$$

The impurity concentration determines the contact resistivity with highly doped semiconductors. In this case the contact resistivity is changed exponentially by a factor of $\varphi_{R_{P}}/\sqrt{N_{D}}$ and it is determined by the equation:

$$\rho_{c} = \left[\frac{A\pi q}{kT\sin(\pi_{C1}kT)}\exp\left(-\frac{\varphi_{Bn}}{E_{oo}}\right) - \frac{A_{C1}q}{\left(c_{1}kT\right)^{2}}\exp\left(\frac{-\varphi_{Bn}}{E_{oo}} - c_{1}V_{n}\right)\right]^{-1},$$
(5)

where A=A*T² and

$$c_1 = \frac{1}{2E_{oo}} \ln \left[\frac{4\varphi_{Bn}}{V_n} \right].$$

The quality and reliability of the ohmic contacts have been evaluated by the behaviour of the main characteristic parameter, the contact resistivity. According to the definition of the contact resistivity it could be present as the contact resistance R_c multiplied by the contact area S:

$$\rho_c = R_c . S \tag{6}$$

Several methods for contact resistivity measurement are known: two probes method, differential method, extrapolation method, method of the interface probes, four probes method and Transmission line model method (TLM). TLM method is the mostly used method because it combines a low measurement error with a possibility of I-V characteristic linearity determination and low sizes of the test structures. Depending on the contact shape in the test structure the TLM method has two modifications, linear (Berger, 1972) and circular (Marlow & Das, 1982). The linear TLM method allows promptly determination of the contact resistivity despite that formation of mesa structures is needed. Formation of mesa structures is not necessary with the circular TLM method; however it is applicable at very low sheet resistance of the metals only. The values of the contact resistivity presented herein are determined using a linear TLM method.

As follows from the theory, two basic approaches could be used to create ohmic contacts: by increasing the semiconductor doping level and/or by decreasing the barrier height (Fig. 1).

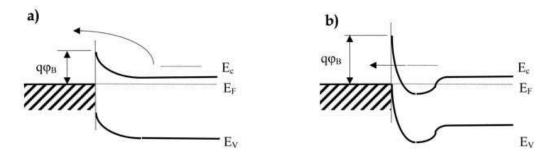


Fig. 1. A zone diagram of an ohmic contact with a) low barrier height and b) high doping level.

It is difficult to obtain low resistivity ohmic contacts to p-type wide band-gap semiconductors due to the high electron affinity and high width of the band-gap. For instance, the electron affinity of SiC and GaN is 3.3 eV and 1.84 eV, respectively. For the mostly used SiC polytypes, the band-gap width is in the interval 2.3-3.2 eV, while for GaN it is 3.44 eV for wurtzite polytype and 3.2 eV of the zinc-blended structure. Hence, a very high Schottky barrier is formed at the interface metal/p-type (SiC, GaN). A metal does not generally exist with a work function enough to yield a low barrier at the interface. In such cases the technique for making ohmic contacts involves the establishment of a heavy doped surface layer such as metal/p⁺-p contact by various methods, such as shallow diffusion, alloy regrowth, in-diffusion of a dopant contained in the contact material. Annealing is the mostly used method for obtaining low resistivity contacts. After the metal film deposition the contacts are heated at the corresponding eutectic temperature for an optimal time in an ambient of an inert gas. As a result they are alloyed into the semiconductor or compounds lowering the barrier height are formed at the interface. The development of such methods of the modern microelectronics as molecular-beam epitaxy (MBE), metal-organic chemical vapour deposition (MOCVD) epitaxy and ion implantation allow obtaining high doping

level ($\geq 10^{20}$ cm⁻³) of the epitaxial layers during the growth. By this technique "in-situ" ohmic contacts can be obtained without annealing.

3. Ohmic contacts to SiC

SiC is a material, which exists in over 130 polytypes. Among them only 6H, 4H and 3C are of interest for microelectronics. Between these three polytypes 4H-SiC has been mainly used for microelectronics devices due to the best combination of widest band-gap, highest breakdown voltage and highest electron mobility.

3.1 N-type contacts to SiC

Ohmic contacts with contact resistivity in an order of $10^{-6} \Omega$ cm² have been successfully developed firstly to n-type SiC. Different metals and its compounds such as Cr, Ni, TiN, TiW, W, Ti, Mo, Ta and etc., have been reported as suitable for ohmic contacts with resistivity in the range of $(10^{-2} \div 10^{-6}) \Omega$.cm² (Porter & Davis, 1995; Crofton et al., 1997). In this section the properties of Ni-based contacts to n-type SiC are discussed because Ni has found to be the most appropriate metal for the device application. Ni and some metals such as Mo, Co, and W are found to form silicides in the metallization interface. During annealing of these contacts the reactions occurring at the interface are accompanied by liberation of carbon whose accumulation in the contact layer deteriorates the contact reliability during the device operation. In order to eliminate this unfavourable effect, a contact system consisting of multilayered Ni/Si films in the ratio 2Ni:Si, has been proposed instead of the pure nickel (Marinova et al., 1997). Herein, Ni/n-SiC and multilayered Ni/Si/n-SiC and Si/Ni/n-SiC contacts formed on substrates with a concentration of 1.8x10¹⁸ cm⁻³ (6H-SiC) and 8x10¹⁸ cm⁻³ (4H-SiC) are compared regarding the electrical, thermal and chemical properties. Studies on the electrical characteristics of these contacts have shown that after annealing at 950 °C for 10 minutes, Ni and Ni/Si layers form low-resistivity ohmic contacts to n-type SiC. The value of the resistivity depends strongly on the substrate doping concentration (Fig. 2). The resistivity of the contacts formed on substrates with the same doping concentration does not differ significantly by the contact composition. Values as measured by a linear TLM method have been determined in the interval $(1.6 \div 2.9)x10^{-5} \Omega.cm^2$ for the contacts formed on substrates with carrier concentration of 1.8x10¹⁸ cm⁻³. Increase the doping concentration to 8x1018 cm-3 affects on contact resistivity decrease by an order of magnitude and a value of $2.7 \times 10^{-5} \Omega$ cm² has been measured with these substrates. The calculations show that the contacts with the same substrate doping level of 1.8x10¹⁸ cm⁻³ have a depletion layer width (potential barrier width, respectively) within the range (1.08 ÷ 1.11)x10⁻⁶ cm (Kassamakova-Kolaklieva, 1999). The higher doping concentration causes narrowing the depletion layer width to 6.06x10-7 cm, which results in decrease of the contact resistivity by an order of magnitude.

The mechanism of current transport through the Ni/SiC, Ni/Si/SiC and Si/Ni/SiC can be determined on the basis of the kT/E_{00} ratio. With the contact systems under consideration, a kT/E_{00} ratio of about 1 has been calculated with a doping concentration ranging from 1.7×10^{18} cm⁻³ to 1×10^{19} cm⁻³. This result determines the thermionic-field emission as the main mechanism of current transport through the contacts. The good agreement between the experimentally obtained values of the resistivity and the theoretical dependence on the doping level calculated with a potential barrier height of (0.20 ÷ 0.35) eV confirms the

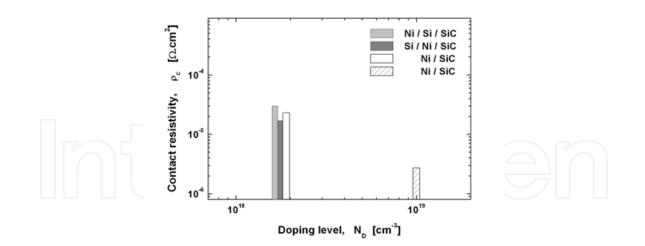


Fig. 2. Dependence of the resistivity of Ni-based contacts to n-type SiC on the substrate doping and the initial contact composition.

thermionic-field character of the current transport in the Ni, Ni/Si and Si/Ni ohmic contacts to n-type SiC (Fig. 3) (Kassamakova-Kolaklieva, 1999).

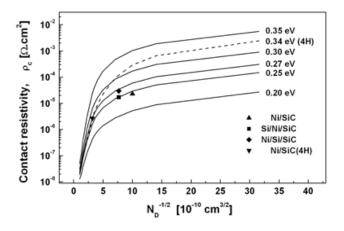


Fig. 3. Comparison of experimentally obtained resistivity values of Ni-based contacts to ntype 6H- and 4H-SiC with theoretical values calculated with different potential barrier heights.

X-ray photoelectron depth analyses (XPS) performed in order to understand the origin of ohmic properties in Ni-based contacts to n-SiC, have shown that the as-deposited polycrystalline nickel layer is homogeneous and a smooth surface is observed. The interface is chemically abrupt with a very thin amorphous layer, probably due to the ion bombardment prior to evaporation. Fig. 4a shows the XPS profile of a Ni/SiC contact after annealing at 950 °C. The Ni2p/Si2p peak ratio, as well as the binding energy of these peaks (respectively 853.2 eV and 99.4 eV), indicate the formation of a nickel silicide with a composition close to Ni₂Si (Grunthaner et al., 1980). Carbon in graphite state (Cls at 284.2 eV) is present in the whole contact layer with a maximal concentration at the interface. At the interface, the Ni2p peak remains at the same position while the maximum of the Si2p and C1s peaks are shifted towards the binding energies corresponding to SiC. The TEM

cross section of the annealed specimen presented in Fig. 5a confirms that the entire nickel layer has reacted to form a nickel silicide. The contact layer contains a lot of Kirkendall voids and its thickness has been increased substantially. The interface is shifted into the SiC, part of which has been consumed to supply Si for Ni₂Si formation. In the area of the original interface, an extremely high number of voids can be found. Quantitative EDS analysis indicates a composition close to Ni₂Si and strong carbon incorporation. Diffraction patterns from different grains could be indexed as the δ -Ni₂Si orthorhombic phase. These results suggest the following mechanism to describe the Ni/SiC contact formation after annealing at optimal temperature of 950 °C: (1) SiC dissociates due to the strong reactivity of nickel above 400 °C; (2) at 950 °C, the Ni₂Si stable phase is formed leading to carbon accumulation both at the interface and in the metal layer (Waldrop & Grant, 1993); and (3) a part of dissociated Si atoms diffuse through the nickel layer and simultaneously Ni atoms diffuse towards SiC until the complete consumption of the deposited nickel layer is realized.

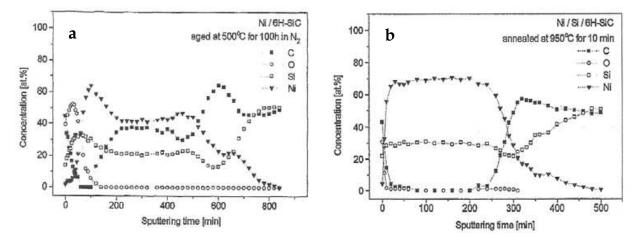


Fig. 4. XPS depth profiles of Ni/SiC (a) and Ni/Si/SiC (b) contacts after annealing at 950 °C for 10 minutes.

The depth distribution of the elements shows that similar profiles are observed for the both contacts, Ni/Si and Si/Ni after annealing at 950 °C for 10 min, when silicon was introduced in the nickel layer in order to prevent the SiC dissociation during the contact formation. XPS profile and TEM micrograph image of the Ni/Si/SiC contact are presented in Fig. 4b and Fig. 5b, respectively. A Ni₂Si layer is obtained as indicated by the binding energies and the ratio of Ni2p to Si2p signal intensity. There is no carbon contained in the silicide layer. At the interface, carbon is still observed but the amount is lower than for the previous Ni contacts. The bright field TEM image of the contact obtained with Si as first deposited layer reveals that the contact layer is uniform, polycrystalline and the δ -Ni₂Si orthorhombic phase is identified. Some Kirkendall voids are still present at the interface but not in the contact layer itself. In the case of the nickel interfacial layer, the contact morphology is similar while a greater number of voids is observed. These results suggest that intentional silicon incorporation in the nickel layer modifies the diffusion processes, which are responsible for the contact formation. In the case of Ni/Si multilayers, Ni and Si mutual diffusion occurs, leading to the stable phase of the nickel silicide, Ni_2Si . The reaction between Ni and SiC at the interface is limited since almost all the nickel is already bonded to the silicon atoms. As a consequence, the SiC decomposition is reduced and only a small amount of carbon is released.

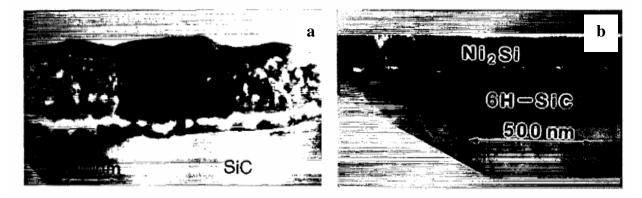


Fig. 5. TEM micrographs of the Ni/SiC (a) and Ni/Si/SiC (b) interfaces after annealing at 950 °C for 10 minutes.

3.2 P-type contacts to 4H-SiC

As it was mentioned, the combination of high electron affinity with wide band-gap in p-type SiC causes high barrier formation at the interface metal/p-SiC, which strongly hampers obtaining low resistivity ohmic contacts. In the case of p-type 4H-SiC a value of the barrier height has been estimated to be over 6 eV. Hence, suitable for p-type ohmic contacts to 4H-SiC could be metals having a work function in order of 7 eV, which is unrealistic. The metals used in microelectronics have work functions between 4 eV and 5.5 eV. For that reason, it is impossible to create ohmic contacts with low resistivity relaying the barrier decrease by selection of a suitable metal only.

A large variety of alloys, metals and compositions have been proposed as suitable for ohmic contacts to p-type SiC. (Porter & Davis, 1995; Crofton et al., 1997) Depending on the contact composition they could be classified in two main groups, 1) Al-based contacts and 2) Al-free contacts. The Al-based contacts consist of Al, its alloys or multilayers one of which is Al. It has been considered that during annealing of these contacts, Al diffuses into SiC, which causes increase of the p-type concentration in the interface layer. As a result, the depletion layer width is decreased and the p-type carriers can tunnel effectively through the potential barrier. Usually, for Al-free contacts refractory metals having a high work function and/or forming compounds, which create low and thin interface barrier, are used.

3.2.1 Al-based contacts to 4H-SiC

Among the all elements (Al, B, Ga, In, Be) used in the present semiconductor technology, Al is the most suitable dopant in the growth of p-type SiC. For that reason, the compositions containing Al have been considered as very appropriate material for p-type ohmic contacts to SiC. Al is the first metal suggested for an ohmic contact to p-SiC. However, the application of pure Al metallization is restricted by formation of pits during annealing which worsen the contact morphology and conductance. In analogy with the silicon technology, Al/Si(1-2 wt.%) composition has been proposed to avoid this problem. Nevertheless, the low diffusion coefficient of Al into SiC requires high annealing temperatures, which enhances the tendency of metal film oxidation and consequently the contact resistivity increases. Therefore, less oxidized refractory metals have been added into the Al-based contact systems. The mostly used metal for this purpose is Ti (Crofton et al.,

1993). The titanium presence in the metallization scheme prevents the Al oxidation and allows its diffusion into SiC. The used thick upper Ti layer acts as a barrier for the Al volatilization observed during the contact annealing. Although other Al-based contacts have been proposed subsequently, the Ti/Al contact still remain the most applied p-type contact in the SiC devices. These contacts could be obtained using an Al-Ti alloy or by subsequent deposition of Al and Ti multilayers (layered contacts).

301

The electrical characteristics of four typical Al-based contacts are presented in Figs. 6. and 7. (Kakanakov et al., 2001; Kolaklieva et al., 2004; Kolaklieva et al., 2007). The contacts are formed on p-type 4H-SiC epitaxial layers with a thickness of 1 µm and a carrier concentration of 3x10¹⁹ cm⁻³. The Au/Al/Si and Au/Ti/Al contacts are multilayered and the films are successively deposited. The thicknesses of the Si, Ti and Al component films were nanoscaled and chosen according to the ratios: Si (2 wt.%) in Al/Si, Ti (70 wt.% and 30 wt.%) in Ti/Al and Al (30 wt.% and 70 wt.%) in Ti/Al before annealing. The total thickness of these films is 100 nm. The same thickness has an AlSi(2 wt.%)Ti(0.15 wt.%) alloy contact. In all contact types a 100 nm thick Au film is deposited as a cap layer.

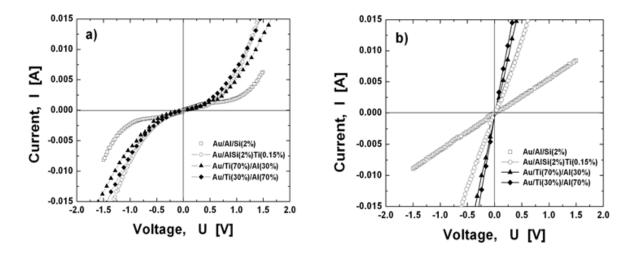


Fig. 6. I-V characteristics of Al-based contacts to p-type SiC: a) as-deposited; b) annealed at an optimal temperature.

I-V characteristics of all as-deposited Al-based metallizations have a shape typical of the Schottky barrier, which determines the rectifying behaviour of the unannealed contacts. They do not differ significantly, which is expectable because of the same substrate doping concentration and the same metal film at the interface. Small difference corresponding to higher potential barrier is observed with the Au/Al/Si contact because of the different element forming the interface with SiC. The initial contact composition and composite ratio influence on the annealing process and dependence of the contact resistivity on the temperature. Fig. 6b presents I-V characteristics of the contacts after annealing at optimal temperature, at which lowest contact resistivity has been observed (Fig. 7). The I-V characteristics of the annealed contacts exhibit various slopes implying different contact resistivities. The smaller slope corresponds to the higher resistivity dependence on the annealing temperature. The addition even of a little titanium amount to the contact composition causes an increase in the annealing temperature at which the lowest contact

resistivity has been obtained, from 700 °C (for Au/Al/Si) to 1000 °C (for Au/Ti/Al). The presence of Ti in the contact composition also affects on the resistivity decrease to a value of $1.2 \times 10^{-5} \Omega$.cm² compared to that of the Au/Al/Si contacts ($2.5 \times 10^{-4} \Omega$.cm²).

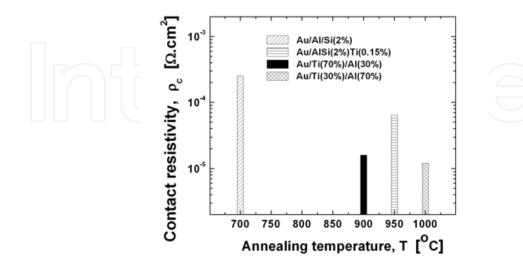


Fig. 7. Contact resistivity obtained for Al-based contacts annealed at optimal temperatures: Au/Al/Si - $2.5x10^{-4} \Omega.cm^2$; Au/AlSITi - $6.4x10^{-5} \Omega.cm^2$; Au/Ti(30%)/Al(70%) - $1.410^{-5} \Omega.cm^2$ and Au/Ti(70%)/Al(30%) - $1.2x10^{-5} \Omega.cm^2$.

The surface morphology of Al-based contacts obtained by Atomic Force Microscopy (AFM) demonstrates strong dependence on the contact composition and weight percentage of each contact component as well as the annealing conditions (Tabl. 1) (Kassamakova et al., 2001; Kolaklieva et al., 2007). AFM images taken from (2x2) μ m² (for Au/Al/Si and Au/AlSiTi) and (10x10) μ m² (for Au/Ti/Al) area reveal the granular structure of the as-deposited contacts. The higher Al amount in the as-deposited contacts causes raising the surface roughness, which originates from the specific feature of Al to form drops during evaporation. After annealing at the optimal temperature the surface roughness increases with the annealing temperature and the Al amount in the contact.

Contact type	Al/Si(2%)	A1Si(2%) Ti(0.15%)	Au/Ti(70%)/ Al(30%)	Au/Ti(30%)/ Al(70%)
R _{MS} (as – deposited contact)	3 nm (2x2) μm²	9 nm (2x2) μm²	8 nm (10x10) μm²	22 nm (10x10) μm²
R _{MS} (annealed at optimal temperature contact)	13 nm (2x2) μm²	16 nm (2x2) μm²	28 nm (10x10) μm²	101 nm (10x10) μm²

Table 1. Surface roughness of as-deposited and annealed at optimal temperature Al-based contacts.

XPS depth analyses of the contact composition and interface chemistry of the as-deposited Al-based contacts reveal an abrupt metal/SiC interface. No interdiffusion between the as-deposited multilayers is observed and well-expressed borders between them are detected. The different compositions and resulting different annealing temperatures led to remarkable

differences in element distribution and interface chemistry of the contacts (Fig. 8). The deposition of silicon between the Al layer and the SiC substrate, and the relatively low annealing temperature reduce the interdiffusion/chemical reaction processes. As a result a significantly more abrupt interface in the Al/Si/SiC contact after annealing at 700 °C has been observed (Fig. 8a). The analysis of the photoelectron spectra shows that interdiffusion and chemical reactions during annealing at 950 °C lead to the transformation of the initial AlSiTi alloy layer (fig. 8b). Due to the catalytic effect of Al at elevated temperatures SiC dissociation occurs at the metal/SiC interface. A part of C reacts with Al to form Al₄C₃ (BE 283 eV), while the other part is registered as graphite (BE 284.5 eV) in the contact layer (0-200 min sputtering). The broadened to the lower binding energy C1s peak (BE 283 eV) after 100 min to 150 min sputtering could be assumed as overlapping peaks of C in TiC and Al₄C₃. A weak Si2p peak determined in the contact layer corresponds to the Si-Si bond. After 200 min sputtering aluminium in metal state only has been detected. The intensity of Al2p peak typical for Al in metal state does not change significantly in the sputtering interval 200-500 min, which suggests diffusion of Al atoms into SiC and widening the interface region (Kassamakova et al., 2001).

Likewise, annealing of the Au/Ti/Al contact changes essentially the element distribution in the contact layer and at the interface as the process determines by the Ti/Al ratio (Figs. 8c and 8d; The different sputtering time is due to the different sputtering ratio, not different contact thickness). The XPS depth profiles allow dividing the contact structure into three regions: surface, film and interface. In both contacts strong Al diffusion to the surface

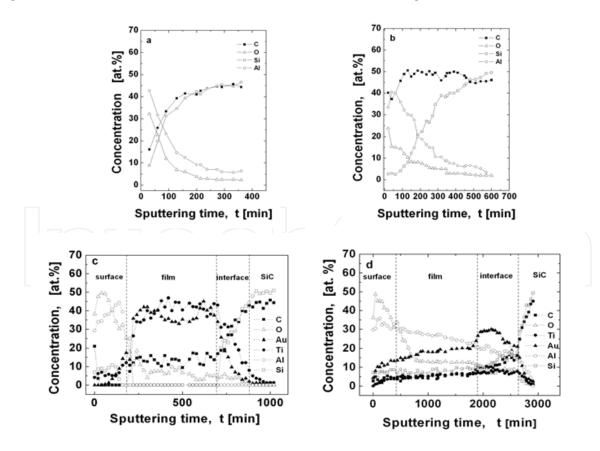


Fig. 8. XPS depth profiles of Al-based contacts: a) Al/Si/SiC; b) AlSiTi/SiC; c) Au/Ti(30%)/Al(70%)/SiC; d) Au/Ti(30%)/Al(70%)/SiC.

promoted by the thermal treatment is obtained. With prolonged sputtering, the Ti/Al=(70/30) wt.% film (Fig. 8c) shows a simultaneous increase in gold and titanium concentrations. The shift of the binding energy of gold in this region up to 84.7 eV is probably connected with the change in chemical surroundings of the Au atoms by Ti atoms and it could be associated with formation of an Au(35at%)+Ti(42at%) alloy. The position of the C1s peak reveals presence of TiC in the film region. Quite a different element distribution is observed for the Ti/Al=(30/70) wt.% contact (Fig. 8d). The film region consists mainly of Au and Al as a decrease in Al and increase in Au concentrations is detected.

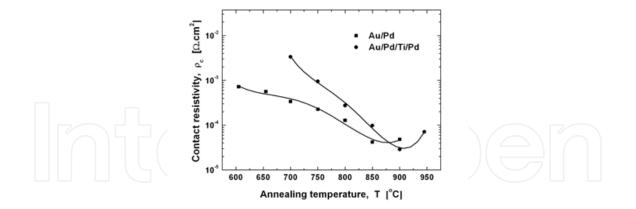
The concentrations of Ti, Si and C remain almost constant and formation of Ti_3SiC_2 compound is possible. Simultaneously a shift of the Au4f peak core level to a higher binding energy (84.2 eV) has been detected up to 1200 min sputtering. This could be associated with change in chemical surroundings of the Au atoms by Al. The formation of an Au-Al alloy is not excluded. Between 1200 and 1800 min sputtering, Au in metal state and formation of TiC is detected. The interface region of the Ti/Al=(70/30) wt.% contact has been found to be narrow. The annealing at 900 °C causes dissociation of the SiC surface and dissociated carbon interacts with Ti forming TiC. The interface region for the contact with a Ti/Al=(30/70) wt.% ratio annealed at 1000 °C is remarkably wider. Along the interface increase of Au, Si and C concentrations has been observed, accompanied by a decrease in Al concentrations. The shift of the Au4f binding energy to the higher values has been determined, which could be connected with silicide formation. Appearance of TiC as a result of the SiC surface dissociation has been also detected. No carbon in graphite state and nonbonded silicon has been obtained (Kolaklieva et al., 2007).

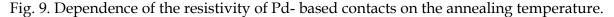
3.2.1 Pd-based contacts to 4H-SiC

Palladium is a metal appropriate for ohmic contacts to p-type semiconductors due to its high work function (5.12 eV). Palladium ohmic contacts are successfully used in GaAs devices. It is known that the silicides of noble metals such as Ir, Pt and Pd are suitable for ohmic contacts to p-type Si. Palladium reacts with SiC at relatively low temperatures (~ 500 °C) and forms silicides, which are considered to be contributory to the barrier height decrease. Besides, recently Pd is a widely used metal in SiC chemical and gas sensors intending to operate at high temperatures. In earlier works Pd is reported as a very promising metal for low resistivity ohmic contacts to p-type SiC (Kassamakova et al., 1999, Kassamakova-Kolaklieva et al., 2003).

The properties of Au/Pd and Au/Pd/Ti/Pd ohmic contacts will be compared in this section. They are deposited on the same substrates as the Al-based contacts. As-deposited Au/Pd and Au/Pd/Ti/Pd contacts show Schottky barrier behaviour. The dependence of the contact resistivity on the annealing temperature is different for both contact compositions (Fig. 9). Ohmic properties for the Au/Pd contacts are observed after annealing at 600 °C and a resistivity of $7.2 \times 10^{-4} \Omega$ cm² has been measured at this temperature. The contact resistivity decreased smoothly with the temperature increase up to 850 °C. After annealing at this temperature a lowest resistivity of $4.2 \times 10^{-5} \Omega$.cm² was obtained for these contacts. The dependence of the resistivity on the annealing temperature is steeper for the Au/Pd/Ti/Pd contacts. Annealing at temperatures of 600 °C and 650 °C does not change the Schottky behaviour. They become ohmic after annealing at 700 °C, but the contact resistivity is still high, $3.3 \times 10^{-3} \Omega$.cm². A lowest reproducible resistivity of $2.9 \times 10^{-5} \Omega$.cm² has been

304





obtained after annealing at temperature of 900 °C. This result shows that addition of the refractory titanium into the contact composition shifts the optimal annealing temperature to the higher values. Further increase of the annealing temperature of both contact types causes a resistivity increase. Consequently, the annealing temperature of 850 °C and 900 °C can be accepted as optimal for ohmic properties formation of the Au/Pd and Au/Pd/Ti/Pd contact composition, respectively.

The different annealing techniques cause different surface morphology of the Pd-based contacts. The surface morphology of the as-deposited contacts follows the surface features (terraces) of the SiC substrate with a surface roughness of around 1.2 nm and a mean grain size of around 100 nm. After RTA annealing at temperature optimal for both contact types the surface reveals an altered granular structure of the metals. Both grain size and surface roughness are increasing to values of 1-3 μ m and 50-100 nm, respectively (Fig. 10 a, b). The annealing in a resistance furnace leads to improved surface morphology and contact properties. The surface roughness (RMS=13 nm) and the mean grain size (150 nm) are smaller (Fig 10 c). However, in this contact structure a strong interdiffusion occurs as can be seen in the AFM image of a scan across the border of a contact pad (Fig. 10 d), where the initial step height between SiC surface and contact pad almost vanishes.

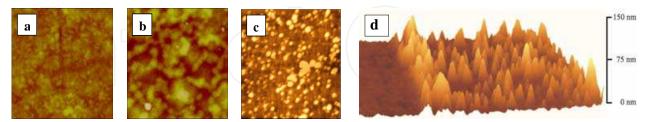


Fig. 10. AFM images: ((25x25) μ m², z-scale 1 μ m) of RTA annealed Au/Pd/SiC contacts at 850 °C (a) and Au/Pd/Ti/Pd/SiC at 900 °C (b); of RFA annealed Au/Pd/Ti/Pd/SiC contacts at 900 °C - 2D image (5x5 μ m², z-scale 50 nm) (c); and 3D image (10x10) μ m² across the border between an annealed contact pad and the SiC substrate (d).

The XPS depth profile of the as-deposited Pd/SiC and Au/Pd/Ti/Pd/SiC contacts show a steep interface metal/SiC as well as steep interfaces between the metals forming the contact composition (Kassamakova et al., 1999; Kolaklieva et al., 2004). After annealing at an optimal temperature the contact composition changes completely (Fig.11). Annealing of the

Pd/SiC contact at 700 °C initializes dissociation of SiC surface in the presence of Pd atoms. The released Si atoms interact with palladium to form palladium silicide while the dissolved carbon atoms start to accumulate at the interface. The XPS spectra have established the presence of the two palladium silicides Pd₃Si and Pd₂Si together with carbon in graphite state distributed in the whole contact film. As a result, the SiC interface is shifted into the SiC bulk, since a part of the original interface is consumed to supply Si for the Pd₃Si formation. After annealing of the Au/Pd/Ti/Pd contact, a new contact composition has been obtained. The contact layer consists of Au in a metal state, unreacted Pd, palladium rich silicide (Pd₃Si) and TiC, while the interface layer is composed of a less Pd-rich silicide (Pd₂Si). As in the Pd/SiC contact a part of the original interface is consumed due to the partial dissociation of SiC to Si and C. Again, the free Si atoms interact with Pd to form Pd₂Si in the interface near region and Pd₃Si in the more remote contact layer, while the dissolved C atoms react with Ti and TiC is formed. Due to the presence of Ti in the contact composition, the carbon resulting from SiC dissociation during annealing is completely consumed. It should be noted that in contrast to the Pd/SiC contact, no carbon in graphite state has been observed in the annealed Au/Pd/Ti/Pd contact. The absence of free C in the annealed contact causes improvement of the contact stability during the long-term treatments and at high operating temperatures. The presence of Au and Pd in metal state contributes to the good contact conductivity.

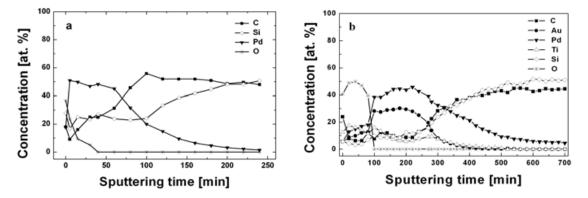


Fig. 11. XPS depth profiles of Pd-based contacts: a) Pd/SiC annealed at 700 °C and (b) Au/Pd/Ti/Pd/SiC annealed at 900 °C.

3.3 Thermal stability of n- and p-type ohmic contacts to SiC.

By contrast with the Si and GaAs devices, which operating temperature is limited by the electronic properties of the semiconductor material, the maximum operating temperature of SiC and III-nitride devices is limited by stability of the contacts. Some device parameters such as response time, output power and etc. depend strongly on the ohmic contact resistivity and its stability at high operating temperatures. Therefore the contact reliability at high temperature treatment is considered as the critical factor determining their power application.

The thermal stability of the contacts consists in their parameters remaining unchanged under the effect of the temperature. This property is investigated on the basis of the behaviour of a physical or electrical parameter characterising the contact under the effect of the temperature. For ohmic contacts such parameter is the resistivity. Usually, the thermal stability of ohmic contacts is investigated for long time treatment at fixed temperatures (ageing test) and by the dependence of the resistivity on the dynamically increasing temperature (temperature-dependence test).

In this section the thermal properties of Ni-based, Al-based and Pd-based ohmic contacts to SiC are presented (Kakanakov et al., 2004; Kolaklieva et al., 2004; Kassamakova-Kolaklieva et al., 2003). The effect of the long term ageing of the contacts on the electrical properties has been studied by heating at 500 °C, 600 °C and 700 °C for 100 hours at each temperature. In fixed time intervals the contacts are cooled to room temperature and the contact resistivity is measured. The results from this study are summarized in Fig.12. All contacts show nonessential change of the resistivity during 100 hours ageing at 500 °C. Both Pd-based contact types have demonstrated good thermal stability at 500 °C heating for 100 hours. Increase of the ageing temperature to 600 °C results in different contact behaviour. A significant effect of the thermal treatment at this temperature is observed on the electrical properties of the Au/Pd contacts. After 24 hours heating their contact resistivity increases to a value of 1.4x10-4 Ω .cm2. Further heating at this temperature does not deteriorate them. On the contrary, the Au/Pd/Ti/Pd contacts show excellent thermal stability during ageing at 600 0C and 700 0C. The improved thermal stability of Au/Pd/Ti/Pd ohmic contacts can be explained by formation of a thermodynamically stable contact configuration during annealing. The annealing of the Au/Pd contacts results in formation of Pd₂Si at the interface. Pd₂Si is the Pd-richest silicide, which is in thermodynamic equilibrium with SiC. Therefore it is considered as a metallization to SiC stable during prolonged thermal treatments. However, the formation of palladium silicides during annealing leads to the accumulation of free C within the contact layer, which is responsible for the observed instability of Au/Pd contacts during the long term ageing at higher temperatures. During annealing of the Au/Pd/Ti/Pd contacts two processes run: formation of Pd₂Si at the interface and reaction between the titanium and the free carbon in the contact layer. The latter leads to the formation of the thermodynamically stable TiC compound phase and reduction (or total use up) of the free C in the contact layer, which results in improving of the thermal stability of the contacts.

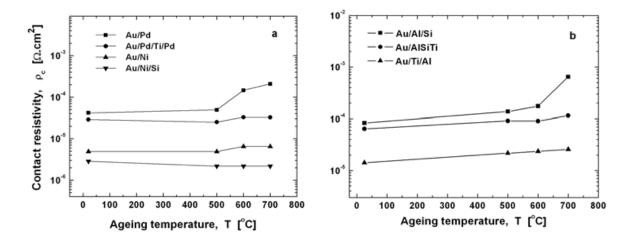


Fig. 12. Dependence of the contact resistivity on the long-term temperature treatment of: (a) Ni-based and Pd-based contacts, and (b) Al-based contacts.

Increase of the ageing temperature to 600 °C causes a very small rise of the resistivity of the Au/Al/Si contact. The resistivity of both contacts, Au/Al/SiTi and Au/Ti/Al, remain

practically the same during the whole time interval at this temperature. During heating at 700 °C, the Au/Al/Si contact resistivity increases continuously to a value of $6.4x10^4 \ \Omega.cm2$ measured after the 100th hour. Slight increase of the resistivity from $9.1x10-5 \ \Omega.cm2$ to $1.2x10-4 \ \Omega.cm2$ is noticed for the Au/AlSiTi contact with the same test. No practical changes in the contact resistivity are detected when the Au/Ti/Al contact is subjected to ageing at 700 °C for 100 hours. The addition of Ti to the contact composition improves its thermal and power properties. This effect is less pronounced in the Au/AlSiTi contacts because of the very small Ti amount in the contact composition. Due to the higher Ti concentration the carbon resulted from the SiC dissociation during annealing is completely consumed and TiC is formed in the contact layer. The absence of C in graphite state is the main factor, which ensures the stability of Au/Ti/Al contact during the ageing up to 700 °C.

The resistivity of Ni-based contacts remains practically the same in the whole time interval at these temperatures. Small instability has been observed with Au/Ni contacts after ageing at 600 °C, but the resistivity remains still low. The observed excellent thermal stability of these contacts is due to the formation of the chemically stable interface with the semiconductor and a stable contact composition of Ni₂Si.

In the temperature-dependence test the measurements have been proceeded at a temperature increasing smoothly from 25 $^{\circ}$ C to 450 $^{\circ}$ C in air. This study gives information on the contact reliability at the corresponding operating temperature as the contact resistivity has been measured during the heating. For the temperature-current treatment, a current with a pre-set density of 10³ A/cm² is supplied for a fixed time at a constant temperature (up to 450 $^{\circ}$ C). This test has been also performed in air and contact resistivity is measured at the corresponding temperature. The results from the two tests are presented in Fig. 13.

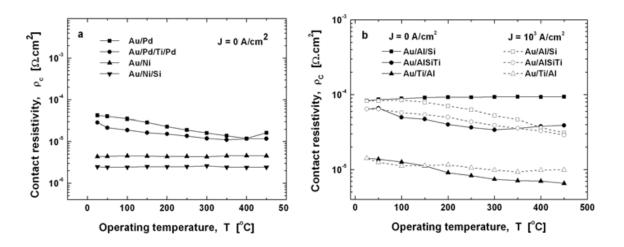


Fig. 13. Dependence of the contact resistivity on the operating temperature and supplied power of: (a) Ni-based and Pd-based contacts, and (b) Al-based contacts

Au/Pd/Ti/Pd contacts have demonstrated better stability at operating temperatures in the interval 25 °C – 450 °C in air. For the Au/Pd contacts the contact resistivity decreases twofold as the temperature increased from 25 °C to 450 °C. Similarly, the contact resistivity of the Au/Ti/Al contact decreases with temperature, however at a slow rate. A slow rate decrease is also observed with the Au/AlSiTi contacts from 25 °C to 300 °C. Further

temperature increase to 450 °C causes increase of the resistivity of these contacts. However, the resistivity value measured at 450 °C is still lower than this one determined at 25 °C. The resistivity of the Au/Al/Si contact remains practically the same at all temperatures from 25 °C to 450 °C. All Al-based contacts have shown a resistivity decrease when a current with a density of J=10³ A/cm² is supplied during the heating. The Ni-based contacts do not change the resistivity during this treatment. After the test is completed and the samples are cooled down the contact resistivity is measured again at 25 °C. The contact resistivity obtained does not differ from the values measured for each contact type before the test.

4. Ohmic contacts for HEMTs based on GaN/AIGaN heterostructures

For the last years III-nitrides have been received great attention as a material having big potential for short-wave optoelectronic as well as RF and power microelectronic device applications. High electron mobility transistors (HEMTs) based on AlGaN/GaN heterostructures are very appropriate for high frequency and high power devices because of the intrinsic material properties such as wide band gap, high breakdown field, and high electron saturated velocity. The low resistivity, excellent reliability at elevated temperatures and good reproducibility of the ohmic contacts are critical factors, which limit the optimum HEMT performance. Besides these requirements, the smooth surface morphology is essential to facilitate sharp edge acuity for short channel devices. Large variety of metal schemes have been proposed and studied as ohmic contacts to AlGaN/GaN HEMTs. Among them Ti/Al-based system has become the conventional widely used ohmic contacts. Such metal scheme could be described as Ti/Al/X(Ni, Ti, Mo, Pd, Pt)/Au.

Multilayered Ti/Al/Ti/Au metal films are one of the mostly used metallizations for obtaining ohmic contacts to HEMTs (Fig. 14a) (Kolaklieva et al., 2008). In the device technology, it is known that Al tends to ball up during contact annealing. This behaviour results in a rough surface morphology of the Ti/Al-based contacts. The first Ti layer being in intimate contact with the GaN or AlGaN interface takes essential role in ohmic properties formation during annealing. Besides, during annealing of these contacts Al reacts with Ti forming Ti_xAl_{1-x} alloys, whose presence in the contact contributes to the contact conductivity. Therefore, investigations have been carried out toward a search for the appropriate initial ratio between the former Ti layer and subsequent Al film (Ti/Al) (Fig. 14b), which enables obtaining low resistivity ohmic contacts with a smooth surface.

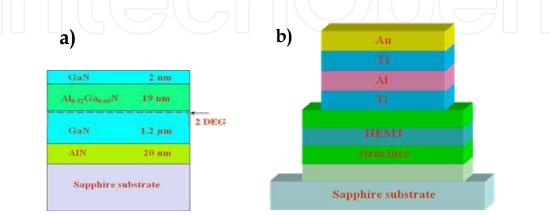


Fig. 14. Schemes of: a) a HEMT structure, and b) an as-deposited contact.

I-V characteristics of all as-deposited Ti/Al/Ti/Au metallizations coincide completely because of the same carrier concentration of the upper GaN layer and the same Ti interface metal layer (Fig. 15a) (Kolaklieva et al., 2009). They have a shape typical of the Schottky barrier, which determines the rectifying behaviour of the contacts. After annealing at temperatures higher than 700 °C the I-V characteristics become linear indicating ohmic contact properties. The I-V characteristics of the Ti/Al (30/70 wt.%) and Ti/Al (50/50 wt.%) contacts coincide completely (Fig. 15 b). This result is expectable because these contacts show the same resistivity after annealing at optimal temperature (Fig. 16a). The I-V characteristic of the Ti/Al (70/30 wt.%) contact exhibits smaller slope implying higher resistivity, which is confirmed by the TLM measurements (Fig. 16 a). For the Ti/Al (30/70 wt.%) and Ti/Al (50/50 wt.%) contacts, ohmic properties have been obtained after annealing at a temperature as low as 700 °C, but the contact resistivity is still high, especially for the contact with higher Ti content. For the Ti/Al (70/30 wt.%) contact, ohmic properties have been observed after annealing at 750 °C. The behaviour of the three contact compositions does not differ essentially in character. There is a tendency to shift to higher

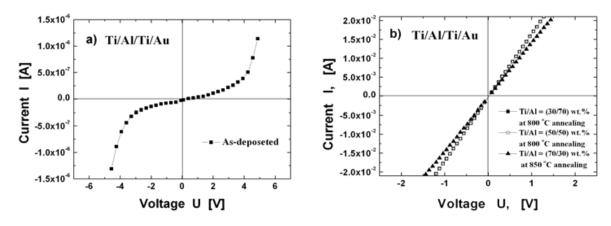


Fig. 15. I-V characteristics of as-deposited (a) and annealed at optimal temperature (b) Ti/Al/Ti/Au contacts with a different Ti:Al ratio.

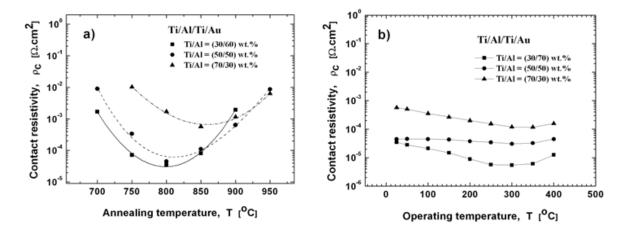


Fig. 16. Dependence of the resistivity of Ti/Al/Ti/Au contacts with a different Ti/Al ratio on the annealing temperature (a) and operating temperature (b).

optimal annealing temperatures with increasing Ti content in the former-Ti/Al layer, which is expectable. The contact resistivity of the Ti/Al (30/70 wt.%) and Ti/Al (50/50 wt.%) contacts decreases smoothly to 800 °C, at which temperature it reaches a minimum value of $4.2x10^{-5} \Omega$.cm² and $4.4x10^{-5} \Omega$.cm², respectively. For the Ti/Al (70/30 wt.%) contact, the lowest resistivity of $5.7x10-4 \Omega$.cm² is measured after annealing at 850 °C. Further increase of the annealing temperature causes increase of the contact resistivity. This resistivity increase could be explained by out-diffusion of Ti and Al to the Au layer and their oxidation at the contact surface, which processes are intensified at high temperatures. The presence of aluminium oxide at the surface has been detected by XPS analysis, which confirms this suggestion.

The investigation on the thermal properties of the three types of contact compositions has been performed in air at a temperature increasing smoothly from 25 °C to 400 °C. Obviously, different initial contact composition causes different thermal behaviour (Fig. 16 b). The best stability shows the contact with Ti/Al ratio of 50/50 wt.%. Its resistivity practically does not change up to 350 °C. Both other contact compositions exhibit smooth decrease of the contact resistivity with temperature increase. A fourfold resistivity drop is found to occur over the whole temperature interval for the contact with Ti/Al ratio of 70/30 wt.%, while six fold resistivity drop of the Ti/Al (30/70 wt.%) contact follows heating under the same conditions. This result shows that higher Ti content causes enhanced stability at operating temperatures up to 400 °C in air.

AFM measurements (Fig. 17) reveal that the surface strongly roughens upon annealing and randomly distributed hillocks appear in dependence on the Ti/Al ratio. It is found that the root mean square (R_{MS}) roughness and the grain size depend on the Al amount in the contact layer. Higher Al percentage in the former-Ti/Al layer causes rising the roughness. R_{MS} surface roughness of 17.3 nm and 15.9 nm is determined for Ti/Al (30/70 wt.%) and Ti/Al (50/50 wt.%) contacts, respectively, after annealing at 800 °C. Lowering the Al content affects on decrease of the grain size from 180 nm to 140 nm as well. Further increase of the Ti/Al ratio leads to a lower roughness of the surface and a smaller grain size of the contact system, even after annealing at temperatures as high as 850 °C. R_{MS} of 12.8 nm and grain size in the interval 110-130 nm are measured with Ti/Al (70/30 wt.%) contacts. The results obtained from AFM examination of contacts with a varying Ti/Al ratio in the former layer have shown that decrease of the Al content improves the surface morphology. The same effect of the Al content has been observed in ohmic contacts to SiC.

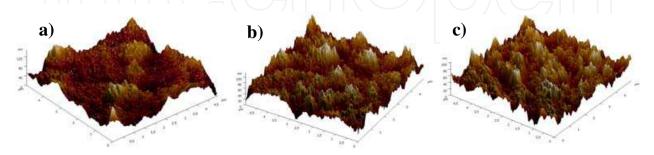


Fig. 17. AFM 3D image of (5x5) μ m² surface area of a Ti/Al/Ti/Au contacts annealed at optimal temperature with a Ti/Al ratio of: (a) - (30/70) wt.%, (b) - (50/50) wt.% and (c) - (70/30) wt.%.

The different initial Ti/Al ratio and the resulting different annealing temperatures lead to remarkable differences in element distribution and interface chemistry of both ohmic contacts as well. The element depth distributions for the Ti/Al (50/50 wt.%) contact after annealing at 800 °C and Ti/Al (70/30 wt.%) contact after annealing at 850 °C are presented in Fig. 18. The profiles reveal intermixing of Al, Ti, and Au layers. In both contacts, strong Al diffusion to the surface induced by the thermal treatment is observed. The surface region of the Ti/Al (50/50 wt.%) contact consists mainly of Al and Au. Going into the depth a gradual decrease in Al and increase in Au concentrations is detected. The binding energy of Au4f7/2 at 84.6 eV is close to that obtained for AlAu₂ alloy. A significant amount of N and smaller amounts of Ga and Ti are found in the region below the gold layers. This is clearly a result of N and Ga outward diffusion towards the surface. Since the measured binding energies of N1s and Ti2p peaks (396.8 eV and 454.8 eV, respectively) correspond to that obtained for TiN, it might be suggested that the diffused N reacts with Ti to form TiN. The depth profile also reveals that during the annealing Al diffuses through the Ti and GaN layers to the interface with AlGaN. The binding energy of Al2s peak here is 119.0 eV, which corresponds to Al in the metal state. At the interface with the AlGaN layer the Al2s peak is broadened and exhibits second maximum at 122.0 eV, which is characteristic of AlGaN. In the surface layers of the Ti/Al (70/30 wt.%) contact predominantly Al in the form of Al₂O₃ is detected (Fig. 18b). Its concentration sharply decreases going into the depth of the layers. This is followed by a strong increase of the gold concentration, which suggests that the thicker Ti layer is more effective barrier against gold diffusion to the interface. The binding energy value of the Au4f7/2 peak near to the region rich in Al is 84.6 eV but decreases to 84.1 eV, into the depth of the contact. The higher annealing temperature results in enhanced outward diffusion of N and Ga toward the surface. The diffused nitrogen reacts with Ti and forms TiN that is evidenced by the measured binding energies of N1s and Ti2p peaks. The most significant difference as compared to Ti/Al (50/50 wt.%) contact is the higher concentration of Ga in this region (20% vs. 10 %), which is probably due to the higher diffusion rate of gallium at 850 °C.

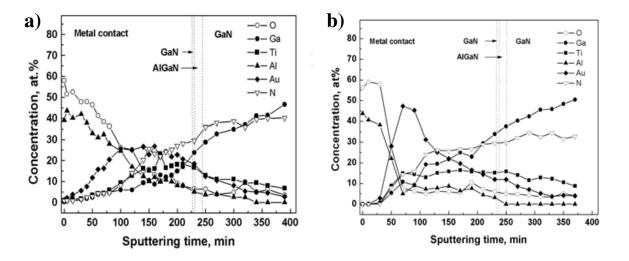


Fig. 18. XPS depth profiles of Ti/Al/Ti/Au contacts annealed at optimal temperature with a Ti/Al ratio of: (a) – (50/50) wt. % and (b) – (70/30) wt. %.

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312

The AFM analysis shows improvement of the surface morphology and narrowing the contact periphery with a decrease of the Al amount in the former-Ti/Al layer. The lowest $R_{MS} = 12.8$ nm of the surface has been achieved for the Ti/Al (70/30 wt.%) contact after annealing at 850 °C. However, the higher annealing temperature enhanced the interdiffusion of the components and the tendency to oxidation of Ti and Al. As a result this contact composition exhibits the worst contact resistivity. Consequently, a compromise regarding the choice of the appropriate composition for ohmic contact to GaN/GaAlN HEMT structures should be made.

5. Summary

The study of ohmic contacts to wide band-gap semiconductors proves that when metal/semiconductor contacts are deposited, they commonly result in rectifying Schottky contacts which barrier height inhibits current flow across the metal/semiconductor interface. There are four primary variables which control the Schottky barrier height at metal/semiconductor interfaces: the work function ϕ_m of the metal; the crystalline or amorphous structure at the metal-semiconductor interface; the diffusion of metal atoms across the interface into the semiconductor; and, the outermost electronic configuration of the metal atoms. Otherwise, there are several constants and properties characterising the wide band-gap semiconductors which postulate the specific approach used for formation of ohmic properties of the metal/semiconductor interface: the high electron affinity, the wide forbidden zone, and low diffusion coefficient of the most metals. Consequently, it is almost impossible to form ohmic properties, relying only to the choice of a metal with suitable work function and metal diffusion into the semiconductor during annealing. Therefore in the case of ohmic contacts to wide band-gap semiconductors metallization schemes have been chosen so as to form intermediate layer at the interface, which could decrease the barrier height and/or narrow the depletion layer at the semiconductor interface. In these cases, heat treatment results interfacial compounds, such as metal/compound/ semiconductor contacts. In these contacts, the metal/semiconductor interface is eliminated and replaced by new interfaces, a metal/compound and a compound/semiconductor interface. The resulting barrier height ϕ_B is not longer dependent on the surface properties of the semiconductor or metal work function. Instead, it depends upon the difference in electron affinity and work function between the metal/compound and compound/ semiconductor. As a result, contacts can be reproducibly formed with a predictable ϕ_B . In the case of Ni-based and Pd-based contacts to SiC such compound is nickel silicide and palladium silicide, respectively.

On the basis of XPS data the following mechanism of chemical reactions occurring during the formation of ohmic properties may be proposed. In the case of Ni/SiC the contact formation is initiated by the dissociation of SiC surface, due to the strong reactivity of Ni at 950 °C. The nickel atoms at the interface interact with a part of dissociated Si atoms and Ni₂Si is formed. Simultaneously, at the interface nickel atoms diffuse through the mixed Ni₂Si+C layer towards the SiC. Thus, the supply of Ni atoms at the SiC interface continues and the above reactions are repeated to the complete consumption of the deposited nickel layer. Carbon accumulates, both at the interface and in the contact layer. The presence of carbon in the contact layer and at the interface could become a potential source of contact

degradation at very high temperatures. When Ni/Si multilayers (instead of pure Ni) are deposited on SiC, the contact formation is preceded by Ni and Si mutual diffusion in the deposited layer yielding Ni₂Si. The presence of Ni atoms at the interface is a reason for dissociation of SiC to Si and C, after which Ni atoms are bonded to the free Si atoms and form Ni₂Si along with carbon in the graphite state. A smaller amount of carbon is observed at the interface. Low carbon segregation at the interface and an abrupt interface characterise this contact. The mechanism of Ni-based ohmic contact formation is illustrated in Fig. 19. The calculations are made on the base of the measured forward I-V characteristic for the asdeposited contact and the thermionic-field emission transport mechanism in the annealed contacts at doping concentration of 1×10^{19} cm⁻³, T=298 K and an effective electron mass m^{*}_n=0.206m₀ (Kassamakova-Kolaklieva, 1999).

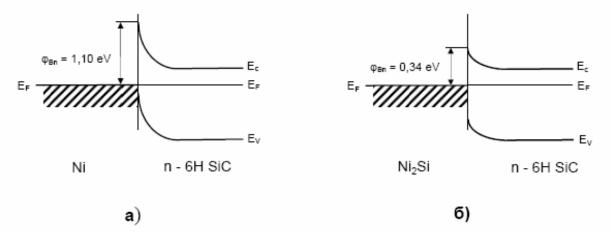


Fig. 19. Energy band diagram of unannealed (a) and annealed at 950 $^{\circ}$ C (b) Ni/n-type 4H-SiC interface.

Annealing of the interface in Pd-based contacts also causes partial dissociation of SiC to Si and C. As a result of this process, the SiC interface is shifted into the SiC bulk since a part of the original interface is consumed. The free Si atoms interact with Pd to form Pd₂Si in the interface near region and Pd₃Si in the more remote contact layer. The formation of these compounds at the interface and in the contact layer, respectively, has been observed for all Pd-based contacts. Consequently, the presence of Pd₂Si at the interface leads to reduction of the barrier height and appearance of ohmic properties, i.e. again lowering the barrier height is realised by silicide formation at the interface (Fig. 20) (Kassamakova-Kolaklieva, 1999).

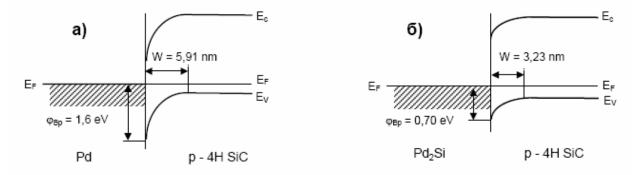


Fig. 20. Energy band diagram of unannealed (a) and annealed (b) Pd/p-type 4H-SiC interface.

The origin of ohmic properties of Al-based ohmic contacts to 4H-SiC depends strongly on the contact composition and annealing temperature. There is no the same mechanism for ohmic properties formation. The low annealing temperature of the Al/Si/SiC contacts decreases the interdiffusion/chemical reaction processes because the dissociation of SiC surface is poor at 700 °C. In addition, the Si layer, deposited on the substrate surface, acts as a barrier for aluminium diffusion. As a result, Al in metal state only is established in the XPS spectra of the Al/Si contacts annealed at this temperature. After ageing of Al/Si contacts at 600 °C for 48 hours areas without a metal film on the contact pads could be seen, suggesting that a part of undiffused Al from the annealed contact layer evaporates during the long term heating, resulting in temperature instability. The increase of the annealing temperature in the AlSiTi contact stimulates a higher interdiffusion/chemical reaction of Al with SiC. Due to the catalytic effect of Al at elevated temperatures SiC dissociation occurs at the metal/SiC interface. The undiffused Al atoms of the contact layer react entirely with the carbon forming a stable compound, Al₄C₃. Indeed, the presence of chemical stable Al₄C₃ compound and the absence of Al in metal state are prerequisite for the improved thermal stability of AlSiTi contacts at high ageing temperatures (Kassamakova et al., 2001). In the case of Au/Ti/Al contacts strong dependence of the contact structure on the Ti:Al ratio and annealing temperature, respectively, has been found out. The TEM analysis reveals that titanium and aluminium silicides and carbides are formed after annealing at 900 °C irrespective of the Ti:Al ratio. However, the Ti:Al ratio affect the kind of silicides and carbides created. In the contact with a Ti:Al ratio of 70:30 Ti₃SiC₂ and TiSi are formed. Although Ti is not in the contact with SiC in the as-deposited structure, it could diffuse through the melted aluminium very fast and reacts with SiC, which is resolved at presence of the molten Al. As a result, the rich on carbon Ti₃SiC₂ phase is formed. The excess Si reacts with Ti to form TiSi and Ti₅Si₃ depending on the Ti amount in the initial contact film. Higher Al content in the initial contact, lower Ti:Al ratio respectively, hinders the formation of ternary Ti₃SiC₂ compound and favours the reactions leading to the formation of binary compounds. Obviously, the higher Al amount makes it more reactive to the carbon than Ti and AlC₄ is detected. In the case of the Au/Ti(70%)/Al(30%) contact the origin of ohmic properties is the formation of ternary Ti₃SiC₂ compound at the interface, which is known to exhibit advantageous metallic properties. However, this compound is not detected in the annealed Au/Ti(30%)/Al(70%) contacts. XPS analysis of this contact has revealed a slight diffusion of Al into the SiC surface after annealing at 1000 °C. It could be supposed, in analogy with the Ti-Al alloyed contacts with the same Al percentage content and annealed at the same temperature (Crofton et al., 1993) that in the annealed Ti/Al layered contacts Al is also distributed like spikes near the SiC surface. Resistivity improvement of the Au/Ti(30%)/Al(70%) contacts after annealing at 1000 °C is due to the Al spikes into SiC. Hence, the origin of the ohmic properties improvement could be explained by the formation of Ti₃SiC₂ compound and enhanced carrier transport by the presence of metal spikes into SiC depending on the initial contact composition and as consequence the optimal annealing temperature (Kolaklieva et al., 2007).

In the case of Ti/Al-based contacts the first Ti layer being in intimate contact with the GaN (or AlGaN) interface takes essential role in ohmic properties formation during annealing. The formation of Ti_xN at the interface is considered important for ohmic behaviour

obtaining. TixN can be grown at the interface between the multilayered metallization by interfacial reactions at temperatures ranging from 250°C (furnace anneal) to 900°C (rapid thermal anneal). The presence of TiN at the interface, with a theoretically predictable work function of 3.74 eV and reasonable electrical conductivities, decreases the barrier height and ohmic properties have been obtained. The formation of TiN at the interface metal /GaN creates nitrogen vacancies in the GaN substrate. These vacancies act as shallow donors, which enhance the doping level at the interface and decrease the width of the depletion layer resulting in decrease of the contact resistivity.

It should be pointed out that besides the interfacial compound, additional alloys and compounds are formed in the contact layer during annealing, which presence aids the better contact conductivity. Obviously, their composition determines by the contact composition before annealing, semiconductor composition and the annealing temperature. Nevertheless, the interfacial reactions are critical to the formation of ohmic contacts on semiconductors, whether they have a large or a small band-gap.

6. References

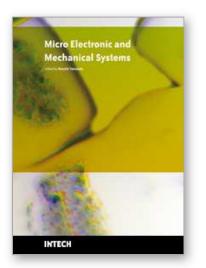
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