Microelectronic Engineering 133 (2015) 73–77

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

AFM study of charging of the Au–n-GaAs contact

A.V. Shmargunov [a,*], V.G. Bozhkov [a], V.A. Novikov [b]

[a] JSC "Scientific Research Institute of Semiconductor Devices", 634034 Tomsk, Russia
[b] "Tomsk State University", 634050 Tomsk, Russia

ARTICLE INFO

Article history:
Received 12 September 2014
Received in revised form 5 November 2014
Accepted 8 December 2014
Available online 15 December 2014

Keywords:
Charging
Contact potential
Kelvin probe
Schottky barrier
Relief modification

ABSTRACT

Effect of charging of structural elements of a metal–semiconductor Au–n-GaAs contact on the behavior of the contact potential difference (CPD) and other properties of the contact is investigated by AFM method. The change of the CPD caused by charging reaches the values of ~0.5 V and depends on the bias value, duration of exposure, scanning speed, and thickness and area of the metal. It is assumed that the above change is mainly due to the accumulation of an induced charge at the metal–semiconductor interface. However, it is not excluded that accumulation of charge occurs also at the grain boundaries of the metal. This is evidenced by the changes in properties of the gold film caused by charging: the rate of the film etching increases. This makes it possible to form a relief on the surface of the metal, which is set by the mode of the probe scanning over the surface of the metal during charging.

1. Introduction

In recent years, a sufficiently large number of papers are devoted to studying the surface and surface potential of semiconductors, including those covered with a dielectric, by atomic force microscopy (AFM) [1–8]. An important area of research is the use of trap charging in structures covered with a dielectric, especially in NOS-structures (nitride-oxide-silicon), for the determination of the trap density and their localization [3–8]. The relevance of such studies is due to the prospects of using the NOS-structures in MOS transistors and memory elements as the gate dielectrics. Main characteristic measured in AFM method using the Kelvin probe force microscopy (KPFM) method is the contact potential difference (CPD) between the probe tip and the surface of the structure under study, which is often referred to as the contact- or surface potential.

It is practically established that a Si_3N_4 layer having high density of deep traps plays the decisive role in the behavior of the surface potential of NOS-structures in the charging process [5–8]. For example, according to [5], local charging of traps by applying the reverse bias of −15 V leads to the change in the value of the local CPD by ~0.5 V. As specified in [5], the trap density at the maximum is $\sim 1.2 \times 10^{12}$ cm^{-2}. An important role in studies of traps is also given to the degree of their lateral localization. From the standpoint of the use of NOS-structures in memory cells, it is important to increase the amount of stored information per unit area. In [5], the minimum linear size of the charged area is about ~0.5 μm. In some of known works, this value is still lower (0.2–0.5 μm) [6,7]. In these studies, the method of scanning capacitance microscopy (SCM) was used for investigations. The smallest known dimensions of the charged region (~50 nm) were obtained by Tzeng and Gwo [8] by using electrostatic force microscopy.

The presence of traps is typical of the metal–semiconductor (M–S) contacts and MIS structures. It is known that the interface and subsurface states in semiconductors (IS and SSS) acting like traps have a significant effect on the characteristics of these structures. First, they can fix the Fermi level, which leads to the independence of the barrier height on the work function of the metal in M–S contacts [9] and screening of the semiconductor relative to the external bias in MIS-structures [10,11]. Second, the IS and SSS in the metal–semiconductor contact being in equilibrium with the semiconductor determine the dependence of the barrier height and, as a consequence, of the ideality factor on the bias voltage. It is shown in [12,13] that the latter circumstance leads to the dependence of these parameters on the contact diameter and temperature. However, there are practically no studies of such states using force microscopy. We note the results [14], where it is found that the CPD measured in the contact with the TiN film depends on the substrate material (Al, Si, Cu and SiO_2), which the film is deposited on. The authors attribute this to the dependence of the film structure on the substrate.

In this work, for the first time, a purposeful attempt is made to apply the method of AFM charging for studying the Au–n-GaAs structure with the Schottky barrier (SB). It is shown that the reverse bias results in a steady change of the CPD reaching significant

* Corresponding author. Tel./fax: +7 (3822) 288122.
E-mail address: tohsh@list.ru (A.V. Shmargunov).

http://dx.doi.org/10.1016/j.mee.2014.12.006
0167-9317/

values (~0.5 V). The factors of the mode and design parameters of the structure influencing its charging are investigated. It is shown that the charging process leads probably not only to a significant accumulation of charge in the interlayer of the M–S contact, IS, and SSS but also to significant changes in the properties of gold. This last is manifested itself in the change of the gold etching rate. All of this allows to form the controlled potential distribution and relief on the surface of gold by setting the mode and topography of scanning.

2. Preparation and investigation of structures

As already mentioned, studies were conducted on the Au–n-GaAs structures with SB. The thickness of the gold coating (h) was varied in the range 50–750 nm. The thickness of the epitaxial n-GaAs film was 0.2 μm. The doping impurity concentration in the n-layer was 4.3×10^{16} cm^{-3}. Immediately before the metallization, the wafers were treated in a solution of sulfuric acid H_2SO_4: H_2O = 1:10. Metallization was performed by electrochemical deposition. On the reverse side of the wafer, an ohmic contact was formed by electrochemical deposition of the AuGe alloy followed by heating. The current–voltage characteristics (CVC) of the contact are characterized by high perfection with the ideality factor of $n \simeq 1.05$.

The reverse voltage (at a current of 10 μA) was in the range from −6 to −13 V, depending on the diameter of the contact (the smaller the diameter, the larger the voltage). Before the AFM studies, the samples were treated in IPA and dried in vacuum. Measurements were performed with an atomic force microscope "Solver HV" manufactured by NT-MDT using the KPFM method. The cantilevers were coated with Pt, the tip curvature radius was 30–50 nm.

This method is based on the registration of the signal proportional to the change of the electric force (F) of interaction between the needle tip of the cantilever (probe) and the surface (in this case, it was gold). During the measurements, AC and DC voltage was supplied between the sample and the probe. The first harmonic of the signal, associated with the interaction force by the following relation, was controlled [15]:

$$F_\omega = \frac{\partial C}{\partial z}(V_{cp} + V_{ind} + V_{st} + V_{\delta i0} + V_{dc})V_{ac}\sin\omega t, \quad (1)$$

where V_{ac} is the amplitude of the AC signal, V_{dc} is the constant bias, V_{ind} is the potential caused by the induced charge, when applying the bias voltage. It is assumed that in the general case, this potential drop is due to the capture of electrons by the interface and near-surface (in the semiconductor) states as a result of a disequilibrium when applying a reverse bias and reverse current flow.

V_{cp} is the contact potential difference between the probe and metal, equal to the difference between the work functions of the probe and material under study. The value $V_{\delta i0}$ corresponds to the potential drop at the M–S interface caused by the difference in the work functions. Initially, it also includes the effect of the charge caused by the defective [16] or metal-induced [17] states that form the Schottky barrier in accordance with the well-known Bardin model [11] (a value of $V_{\delta i0}$ is schematically shown in Fig. 1). In general case, a total potential drop $V_{\delta i}$ at the M–S interface also includes the effect of the charge stored in ISs interacting with the semiconductor [12], as well as the charge adsorbed on the metal and semiconductor surfaces and in an intermediate layer between them. This charge can be related to a certain value of the potential V_{st} (schematically shown in Fig. 1), which is an integral part of the value $V_{\delta i}$ and is ultimately caused by the charge accumulated in the contact during its formation, i.e., by the design and technology of the contact. We note that the value of the potential V_{st} can be caused also by the significant change in the electron affinity of GaAs due to the formation of a negative charge or dipoles with the corresponding orientation [18].

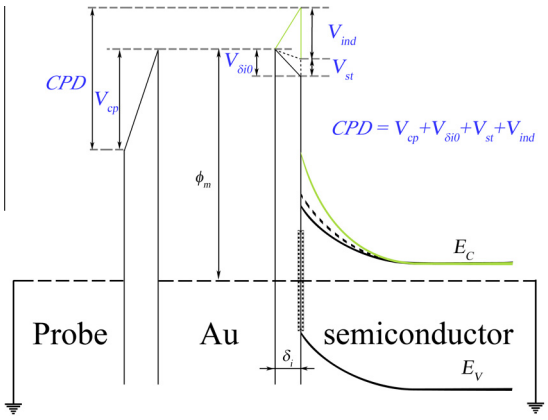

Fig. 1. Energy diagram of the probe-Au–n-GaAs system showing the effect of the potential drops V_{st} and V_{ind}, caused by the accumulated and induced charges, on the value of the measured contact potential difference.

The interaction force F is zero at

$$V_{dc} = -(V_{cp} + V_{\delta i0} + V_{st} + V_{ind}) = \mathrm{CPD}, \quad (2)$$

which allows to determine the CPD. Since the bias source is connected directly to the cantilever, the sign of the measured value V_{dc} should correspond to the sign of the contact potential of gold.

Obviously, in an ideal case of lack of the accumulated and induced charges in the system, the measured value of V_{dc} should correspond to the sum of the theoretical difference V_{cp} between the work functions of the probe and metal and a some value of $V_{\delta i0}$ (see above) characterizing the theoretical difference between the work functions of the metal and semiconductor (Fig. 1).

The charge accumulated in the system (see above) is associated with the adsorption of products of the surrounding and technological environment on the surface of the probe, metal, in the intermediate M–S layer, and possible, at the boundaries of the metal crystals (Au) during the fabrication of the structure (it can be said that it is a naturally accumulated charge). Fluctuations in the value of this charge and associated potential drop V_{st} cause the observed fluctuations in CPD at identical conditions of fabrication of structures.

Unlike to the naturally accumulated charge, the density of an induced charge is increased only on the traps of the structure as a result of application of voltage to the probe-structure system in the contact scanning mode. The states are related with V_{st} and V_{ind} can have one nature. In the process of the charge inducing, the voltage corresponds mainly to the reverse bias on the Au–n-GaAs contact. We changed the value of the applied bias, the scanning speed and the number of scanning cycles of the same area. Then, using the KPFM method, we measured the contact potential distribution over the scanned surface and beyond it. During measurements, the tip-sample distance was kept constant in the range 20–60 nm. Note that in general case, the changes of the accumulated and induced charges may cause a change in the band bending, which is shown in Fig. 1.

3. Results and discussion

AFM images of the relief and CPD of the Au–n-GaAs contact surface and the sections of these images in the vertical plane are shown in Fig. 2. Here, the bias voltage during charging is V_r = −10 V, the velocity of the probe is 20.24 μm/s, and the movement step is 39.22 nm (~2 μs/point). There is no doubt about the

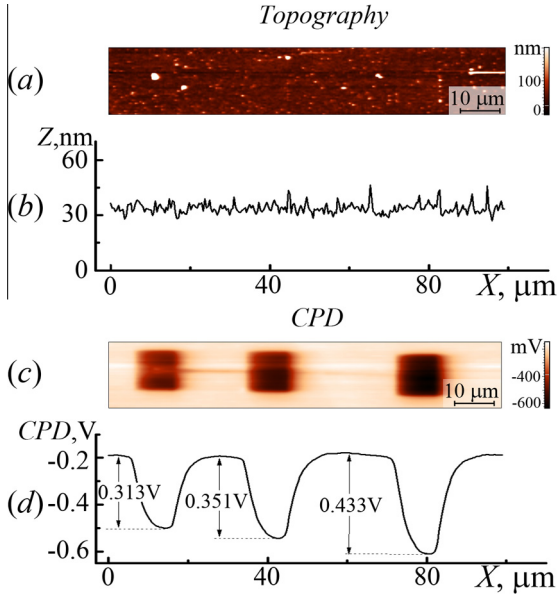

Fig. 2. AFM images of the surface topography and CPD of the gold film on n-GaAs: (a) – image of the gold surface topography, (b) – cross-sectional view of the topography in the vertical plane, (c) – image of the CPD of the gold film, and (d) – cross-sectional view of the CPD in the vertical plane.

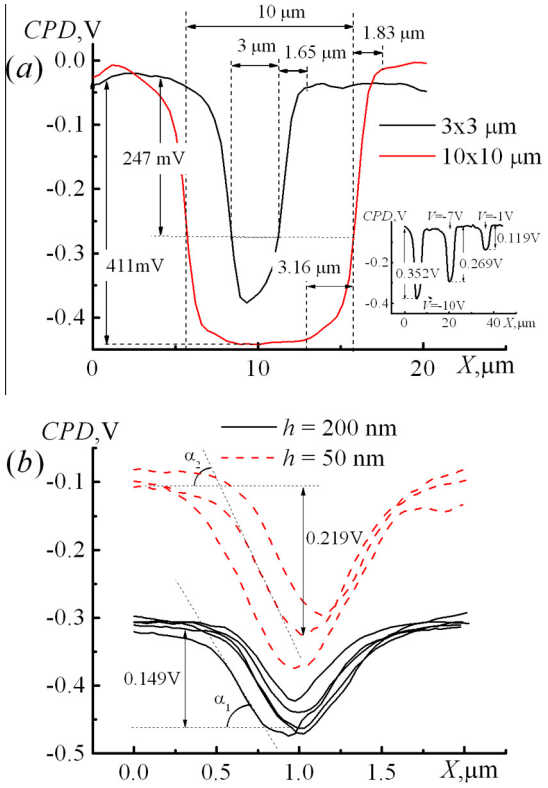

Fig. 3. Dependences of the contact potential difference profiles on the scanned area (h = 50 nm) – (a) and the metallization thickness – (b). In the inset in Fig. 3(a) – the dependence of the CPD on the supplied bias under single scan.

potential change in regions, where charging was carried out (10 × 10 μm). It is obvious that the change of the CPD in the scanned area is equal to the value of the potential V_{ind} caused by an induced charge (see Fig. 1). The first, second, and third regions with the modified potential (left to right) in Fig. 2(c) and (d) correspond to the one, two, or three cycles of charging of the surface area of 10 × 10 μm by the voltage of −10 V, respectively. These data are similar to the well-known studies of NOS-structures [5–8]. The observed changes of CPD are stable enough. Processing of structures in a H_2SO_4:H_2O = 1:10 solution qualitatively does not change the picture. Measurements performed after 6 days showed a decrease of V_{ind} two to three times (from 350 to 100–200 mV). During the first day, the potential was reduced by about 15%.

It follows from Fig. 2(c) and (d) that the value of V_{ind} increases with the scanning time (with the increase of the number of cycles). The same effect is caused by a decrease of the scanning speed and an increase of the reverse bias (the latter is shown in the inset in Fig. 3(a)). Note that the supply of the forward bias changes the CPD in a positive direction. However, the influence of the forward bias is limited by the permissible current of 10 nA in the circuit. As a result, the change of V_{ind} usually does not exceed 50 mV.

The dependence of V_{ind} on the bias at the contact is obviously caused by a fairly wide spectrum of charged states (traps), which is typical also of the NOS-structures [5]. In this case, the greater the disequilibrium (the bias), the more traps are included in the process of capture and the greater the value of the trapped charge, and hence, the value of the potential drop.

Equally clear is the dependence of V_{ind} on the charging time. This dependence is associated with the presence of a wide spectrum of traps with different time constants of capture, and the more the charging time, the greater the probability of capture of charge by the more "slow" traps. In this case, an essential role is played by the "asymmetrical" nature of the trap charging and discharging processes, as follows from the data presented: an average time of charging is 2 μs, whereas an average time of discharging is hundreds of hours. As a result, in the subsequent cycles of charging, the trapped charge and the associated potential drop V_{ind} are further increased.

Due to the fact that during the measurement of CPD by the KPFM method (in the non-contact mode), the bias voltage V_{dc} is applied to the cantilever, as in case of scanning (in the contact mode), the contact potential is also changed under continuous measurements of the same surface area. This effect of charging can be quite noticeable under normal conditions of measurements. For example, fifteen repeated measurements reduce the value of V_{ind} by 50–100 mV (~20%). Under two measurements, this effect does not exceed 7%.

Studies show that the size effect is characteristic of V_{ind}. With decreasing scanned area, an induced potential in the minimum starts to decrease (Fig. 3(a)). As can be easily seen, the "walls" of the dependence CPD(X) do not coincide with the boundaries of the scanned area. They are inclined and begin to intersect starting from a certain charging area (~6 × 6 μm) gradually increasing the minimum value of CPD. At the edge of the chargeable area, the value of V_{ind} does not depend on the size of this area and is 247 mV, Fig. 3(a). The value of "smearing" only weakly depends on the size of the chargeable area (1.65–1.83 μm). Apparently, the presence of an inclination is due to the fact that the charge inducing occurs not only in the vertical direction, but in all directions relative to the probe. The inclined "walls" of the CPD(X) dependences also result in another size effect: as the distance between the scanned areas decreases, the CPD between them cannot reach the value characteristic of the large surface CPD of the metal, i.e., it is lower than this value.

It is interesting to note that, despite a very slow relaxation of "charged" metal surface after the charging, the recharging of the surface with lower bias voltage generates a contact potential corresponding to this bias voltage in the absence of pre-charging. This indicates that in the contact mode, the nonequilibrium processes (charge and discharge processes of defect states in the structure)

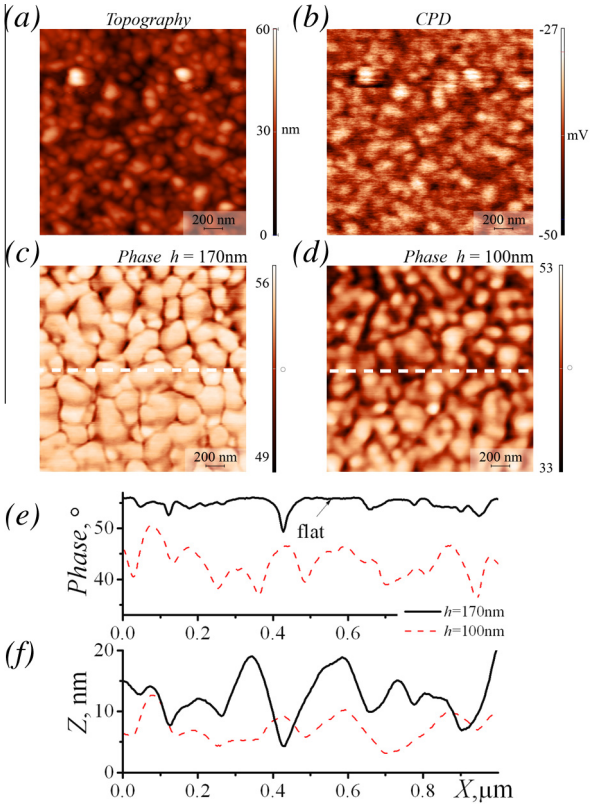

Fig. 4. Surface topography of gold (a) and corresponding image of CPD (b) (h = 50 nm). The phase contrast of the gold films with the thickness of 170 nm (c) and 100 nm (d). Vertical cross-section of the phase contrast (e) and the surface topography (f) for films with different thicknesses.

are sufficiently fast, in contrast to the non-contact mode described above.

One of the most interesting features of charging of the Au–n-GaAs structure in the contact mode is the dependence of the induced potential on the thickness of the SB metallization (Fig. 3(b)). In this case, charging of the structure was carried out by a single line scanning at the bias voltage of −10 V. The CPD profiles were measured in the non-contact mode in the direction perpendicular to the charging line. The results of measurements along some parallel lines are shown. These results draw attention to two effects.

First, an equilibrium contact potential of thicker films is lower than that of thinner films. In our view, it can be associated with a larger negative charge naturally accumulated in the system during growth of thick gold films (see above). Secondly, charging of structures with finer metallization leads to a greater change in the CPD, i.e., to a greater value of the induced potential. This result is quite stable. At least, it is weakly dependent on the type of GaAs pretreatment before the deposition of gold. For example, instead of the above processing before deposition of the metal, GaAs was etched in an $NH_4OH:H_2O_2:H_2O$ = 10:3.5:500 solution for 15 s and dipped in the $NH_4OH:H_2O$ for 30 s. At film thicknesses of 100, 170, and 770 nm, the changes of CPD were 300, 180, and 130 mV, respectively. We can note that the changes of CPD become slower with increasing thickness of the metal. Fig. 3(b) shows that the inclination of "walls" the greater, the smaller the film thickness ($\alpha_2 > \alpha_1$).

A more detailed AFM study of the surface of metal films also leads at least to the two conclusions. First, the relief (structure) of the metallization surface correlates with the relief of the contact potential: the potential corresponding to the grain boundaries of the metal film has a more negative value (Fig. 4(a) and (b)). Second, thick metal films have a more dense packing of grains, as is shown in the phase contrast images in Fig. 4(c) and (d). The phase contrast of the thick film (Fig. 4(e)), despite of a more developed relief (Fig. 4(f)), varies slightly in comparison with that of the thin film. Otherwise speaking, the structure of thin films is characterized by greater friability.

It is difficult to say anything concrete about the mechanism of charging of gold films and the impact of this charge on the CPD. The available results indicate the existence of potential barriers between the grains in polycrystalline films [19,20] associated with the charge trapping. It is possible that in the metal with an accumulated negative inter-grain charge, such macrocharacteristic as the work function is changed. More specifically, the work function of the metal increases the more significant, the greater the accumulated charge.

For the polarized (scanned) surface of gold, another amazing property was found – the change of chemical activity. As it turned out, the etching rate of this surface is substantially higher than that of the conventional gold layers. This was indicated by etching of gold in a solution containing $CH_4H_2S:Na_2S_2O_3{\cdot}5H_2O:K_3[Fe(CN)_6]$ = 50:50:50 (g/L) for 5 s after the charging process. Fig. 5(a) and (b) show the relief of the polarized and etched area of the surface and the cross-section of this relief.

The dependence of the etching rate of the metal surface on its charging makes it possible to controllably form a relief of the metal surface (by changing the potential and/or duration of polarization), as shown in Fig. 5(c) and (d). It seems that this property of metal films can have practical importance as a new maskless lithography method. The images of the potential relief formed as a result of

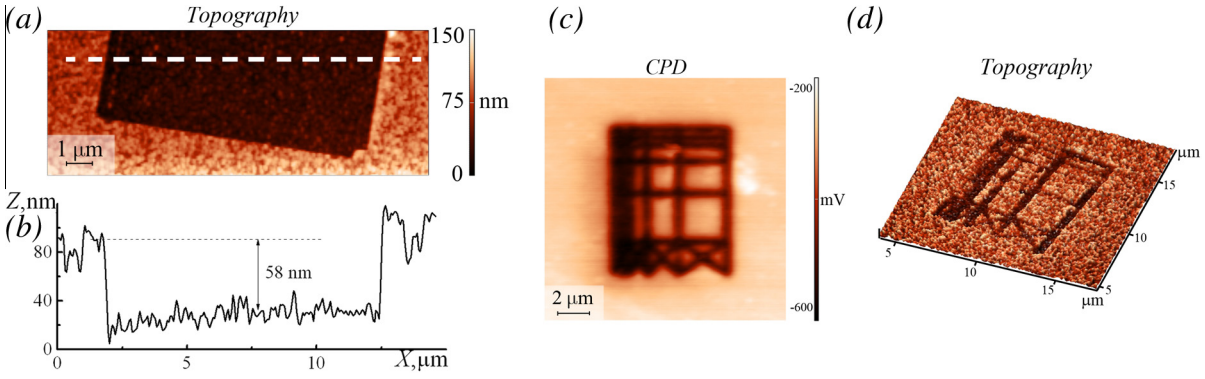

Fig. 5. Dependence of the gold etching rate on the preliminary polarization: (a) – the gold film topography in the scanned and etched area of 10 × 10 μm at V_r = −10 V, (b) – the topography cross-section, (c) – topography of the contact potential after polarization (V_r = −10 V, 15 cycles), and (d) – surface topography after etching.

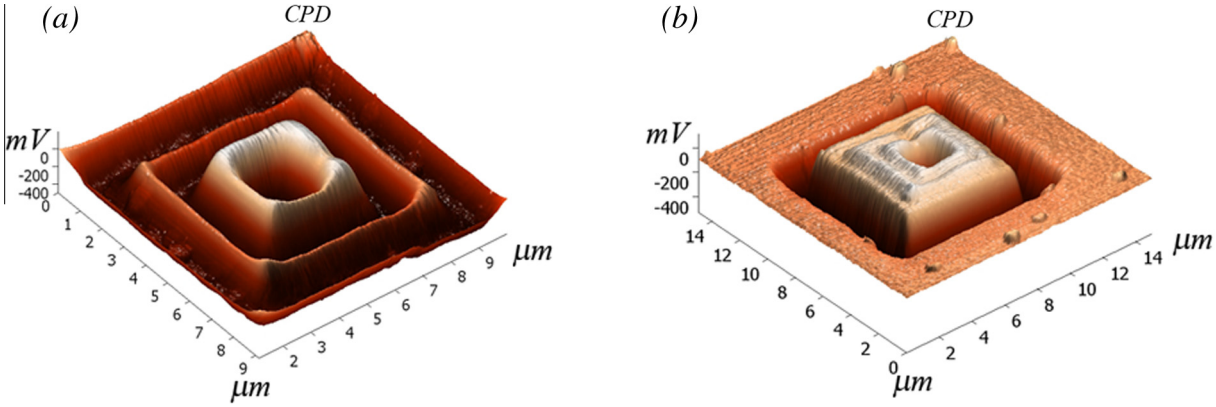

Fig. 6. Images of the CPD formed on the surface of the gold film using different modes of polarization.

polarization are shown in Fig. 6. They indicate the possibility of creating a quite complex relief using a preliminary polarization and subsequent etching.

4. Conclusion

For the first time, a detailed AFM study of the charging processes of Au–n-GaAs structures is fulfilled using the KPFM method. It is shown that scanning of the surface with a cantilever in the contact mode in the presence of the bias on the Schottky barrier contact leads to the charging of the scanned area and to the change in its contact potential (CPD). The effect is generally similar to that observed previously in the NOS-structures and depends on the value of the reverse bias, number of scanning cycles, scanning speed, area of the scanning region, and metal thickness.

It is assumed that an initial (before charging) CPD value is determined not only by the drop of the potential, typical of an ideal probe-Au–n-GaAs system, but also by the adsorption of the charged products of the atmosphere and technological environment, which may generate an additional potential drop V_{st}. In turn, polarization creates a quite controlled potential drop V_{ind} as a result of the charge trapping in the system. It is assumed that these traps are located in the interface region and/or in the subsurface region of the semiconductor and are characterized by the relatively fast charging time (~2 μs) and slow discharging process (hundreds of hours). It is interesting that the polarization effect depends on the metal thickness. This indicates that the metal structure can affect the charging processes. In turn, the metal structure depends on the thickness of metallization. The effect of the metal structure is also supported by the changes in chemical properties of the polarized area of the gold coating. Etching rate of this area increases. This allows to form a quite complex relief on the metal surface using polarization and subsequent etching.

References

[1] N.A. Torkhov, V.A. Novikov, Semiconductors 45 (2011) 69.
[2] O. Ochedowski et al., Nanotechnology 23 (2012) 405708.
[3] M. Chang et al., Appl. Phys. Lett. 94 (2009) 262107.
[4] M. Jaquith, E.M. Muller, J.A. Marohn, J. Phys. Chem. B 111 (2007) 7713.
[5] G. Lubarsky, R. Shikler, N. Ashkenasy, Y. Rosenwaksa, J. Vac. Sci. Technol. B 20 (5) (2002) 1914.
[6] R.C. Barrett, C.F. Quate, J. Appl. Phys. 70 (5) (1991) 2725.
[7] Hong et al., Appl. Phys. Lett. 75 (12) (1999) 1760.
[8] S.-D. Tzeng, S. Gwo, J. Appl. Phys. 100 (2006) 023711.
[9] E.H. Rhoderick, R.H. Williams, Metal–Semiconductor Contacts, second ed., Clarendon Press, Oxford, 1988.
[10] H. Hasegawa, M. Akazawa, Appl. Surf. Sci. 254 (2008) 8005.
[11] S.M. Sze, Physics of Semiconductor Devices, second ed., Wiley, New York, 1981.
[12] V.G. Bozhkov, A.V. Shmargunov, J. Appl. Phys. 111 (2012) 053707.
[13] V.G. Bozhkov, A.V. Shmargunov, T.P. Bekezina, N.A. Torkhov, V.A. Novikov, J. Appl. Phys. 115 (2014) 224505.
[14] N. Gaillard et al., Microelectron. Eng. 83 (2006) 2169.
[15] S.B. Kuntze et al., Crit. Rev. Solid State Mater. Sci. 30 (2005) 71.
[16] W.E. Spicer, T. Kendelewicz, N. Newman, R. Cao, C. McCants, K. Miyano, I. Lindau, Z. Liliental-Weber, E. Weber, Appl. Surf. Sci. 33/34 (1988) 1009.
[17] W. Mönch, J. Vac. Sci. Technol. B 17 (4) (1999) 1867.
[18] Tachiki et al., Surf. Sci. 581 (2005) 207.
[19] V.M. Kozhevin et al., Phys. Solid State 45 (2003) 1993.
[20] K. Makihara et al., J. Non-Cryst. Solids 358 (2012) 2086.