Influence of gas discharge plasma on forming process and properties of complex films

Y S Zhidik1,2, T I Danilina1, A A Chistoedova1, E V Zhidik1 and L R Bitner1

1 Tomsk State University of Control Systems and Radioelectronics, 40 Lenin Ave., Tomsk, 634050, Russia
2 V E Zuev Institute of Atmospheric Optics SB RAS, 1 Ac. Zuev Sq., Tomsk, 634055, Russia

E-mail: Zhidikyur@mail.ru

Abstract. In this paper, we present the research results on the formation mechanism of stoichiometric compounds of complex thin films formed by ion-plasma sputtering in reactive gases environment. The kinetics of complex films’ formation and growth is studied as well as the change in characteristics of microelectronics elements formed on the basis of thin films during their electron-ion bombardment.

1. Introduction

At present, with regard to complex films production, the ion-plasma methods are of great interest. They allow production of films with various modifications and composition for a wide range of applications while varying the technological parameters [1].

The main disadvantage of ion-plasma methods is the negative impact of the gas discharge plasma, due to the intense electron-ion bombardment of the deposited films. This can lead to breakdown of dielectric films, the formation of a mobile charge, an increase in fixed charge and the density of surface states [2, 3]. Electron-ion bombardment also adversely affects the characteristics of low-dimensional heteroepitaxial structures used, forming radiation defects in them that cause degradation [4, 5]. At the same time, the degree of impact of electron-ion bombardment depends on the method of realization of the methods for producing films [6].

In this paper, we consider and summarize the research results on the formation mechanism of stoichiometric compounds of complex thin films formed by ion-plasma sputtering in reactive gases environment. The kinetics of their growth is studied, the results of studies of changes in the properties of thin films and substrates during ion-plasma processes are given, and the changes in the characteristics of microelectronics elements formed on the basis of thin films during their electron-ion bombardment are studied.

2. A study of compounds formation mechanism with ion-plasma deposition method of complex films

The first studies conducted by the authors were associated with the development of ion-plasma sputtering methods based on the Penning discharge system and the magnetron sputtering system, which were used to develop technologies for producing insulating and conducting complex films [7]. The films
of oxide and nitride compounds of silicon and aluminum were formed by the method of ion-plasma sputtering of targets in the reactive gases environment (reactive ion-plasma sputtering).

The compounds formation mechanism was studied by sputtering Si and Al targets in the oxygen and nitrogen environment by analyzing the composition of sputtered particles using a modified radio-frequency mass spectrometer, as well as by optical spectroscopy [8]. In the study of the composition of sputtered particles using a mass spectrometer in both neutral and ionized form, the presence of atoms and ions of materials from Si and Al cathodes was shown. However, when spraying silicon in an oxygen atmosphere, the peak of silicon oxide ions SiO\(^+\) is three times the peak of silicon ions Si\(^+\).

The study of plasma using optical spectroscopy showed the presence of bands of nitrogen and oxygen, as well as atomic lines of silicon and aluminum. No bands corresponding to SiN, SiO, AlN, AlO molecules were detected. Consequently, the formation of Si\(_3\)N\(_4\), AlN, Al\(_2\)O\(_3\) compounds occurs on a substrate, where atoms and ions of silicon or aluminum, as well as molecules and ions of a reactive gas enter. In the case of sputtering a silicon target in an oxygen atmosphere, both Si and SiO atoms are sputtered. Additional oxidation to SiO\(_2\) also occurs on the substrate.

Such a difference in the compounds formation mechanism can be explained by taking into account the bond breaking energy Si-O (8.2 eV), Si-N (5.2 eV), Al-O (5.2 eV), Al-N (3.69 eV). As it is known, under the action of ion bombardment, the composition of the target surface (cathode) can change, namely, the introduction of ions of the sputtering gas occurs with the formation of bonds between the implanted ions and the target atoms [9, 10]. Upon subsequent spraying of the formed compound, the bonds may break, especially if the bond breaking energy is small, as in the case of AlN, AlO, SiN, and atomic particles Al or Si will enter the substrate. In the case of high binding energy, for example, SiO, molecular particles constitute a significant or majority of the total sprayed material. In all these cases, the processes on the substrate play an important role in the formation of complex films.

3. Complex films formation mechanisms under plasma exposure

Despite the detrimental effect of electron-ion bombardment on the parameters of semiconductor heteroepitaxial structures, a large number of scientific papers report on the prospects for the deposition of thin-film coatings under conditions of ion-assisted stimulated growth. Thus, it was noted in [11] that the introduction of ion treatment into the magnetron sputtering process leads to the growth of polycrystalline indium oxide films already at a substrate temperature of 50 °C. In this regard, of particular interest is the study of the complex films’ formation mechanism under the conditions of exposure to a gas discharge plasma.

In the framework of such studies, it was found that with increasing Penning discharge power and as the substrate approaches the discharge chamber, the substrate temperature significantly increases. Even with a low discharge power \(W_p = 1.9 \text{ W-cm}^{-2}\), the temperature of the substrate raises from 50 °C to 350 °C as the substrate approaches the discharge from a distance of 20 mm to the boundary of the gas discharge plasma. The time for the temperature to set does not exceed 15 minutes. Heating of the substrate can be attributed to the combined effect of electron-ion bombardment and plasma emission. However, the latter makes a greater contribution to heating, since it is known that up to 70% of the power released at the anode is transferred by plasma radiation when in a Penning discharge [10].

The degree of electron-ion bombardment is determined by the energy of the particles entering the pole and their number. To determine these values, we used probe current-voltage characteristics obtained using a Langmuir probe located near the substrate [12]. The average electron energy measured in this way for devices based on the Penning discharge at a discharge voltage of (600–800) V was 20 eV, and the floating potential was 90 V. In magnetron sputtering systems, the energy of electrons falling on a substrate measured the same way was about 300 eV.

The effect of electron-ion bombardment on thin-film and semiconductor structures was studied with MDM and MIS capacitors. Silicon nitride films prepared by sputtering silicon cathodes in a Penning gas-discharge chamber filled with nitrogen at a pressure of 0.5 Pa served as dielectric capacitors. Aluminum films deposited by thermal vacuum evaporation were used as plates.
Different degrees of plasma impact on the film properties were provided by changing the substrate distance to the gas discharge plasma boundary. The parameters of the MDM capacitors remained almost unchanged with the intensity of electron-ion bombardment that takes place in a Penning gas-discharge chamber in the case of an isolated substrate under a floating potential.

Electron-ion bombardment has a more significant effect on the MIS capacitors’ characteristics. We researched the effect of electron bombardment on the properties of the silicon-nitride silicon interface. For this purpose, capacitance-voltage characteristics were obtained for the case of a floating potential on the substrate and the substrate that was under the potential of the anode (figure 1). It can be seen that an increase in the intensity of electron bombardment (curve 2) leads to the appearance of a large positive charge at the interface and to an increase in the density of surface states. Vacuum annealing significantly reduces the density of surface states, but the positive charge does not decrease.

![Figure 1. The effect of electron-ion bombardment of the substrate on the capacitance-voltage characteristic of the structure: 1 – substrate at floating potential; 2 – substrate at anode potential; 3 – sample 2 after annealing in vacuum.](image1)

The position of the curve 2 depends on the measurement frequency, shifting towards large negative voltages with decreasing frequency. After annealing, the frequency dispersion disappears. The positive charge at the Si-Si₃N₄ interface decreases with decreasing of the current density on the substrate (figure 2).

![Figure 2. The dependence of the voltage of flat zones on the current density on the substrate (the substrate is under the potential of the anode).](image2)

Intensive electron bombardment contributes to the appearance of a significant hysteresis of the volt-farad characteristics, which is especially noticeable when the bias’s change rate is 50 V·s⁻¹. The shape of the hysteresis loop is characteristic of the case of the electrons capture by deep traps in the dielectric [13], which are apparently formed as a result of electron bombardment.

The differences in the formation of reactively sprayed silicon nitride films on a substrate in the presence and absence of electron-ion bombardment are established. In the latter case, a grid electrically connected to the anode was used, which practically eliminated the flow of charged particles onto the substrate. During the formation of reactively sputtered silicon nitride films, as shown by mass spectrometric studies, individual atoms of silicon, nitrogen and a small proportion of Si-N compounds
are fed to the substrate from the sputtered target. At the same time, the molecules of the working gas of nitrogen are adsorbed on it, as well as small amounts of oxygen and water, which are always present in the working chamber. It is known that nitrogen is physically adsorbed on silicon, so a direct reaction of molecular nitrogen with silicon on the substrate is difficult. It is facilitated, as we suggested in [14], by dissociation, excitation and ionization of molecular nitrogen when bombarded by low-energy electrons. The formation of the Si-O bond is possible due to the chemical interaction of molecular oxygen with silicon. However, the oxide content in silicon nitride films is usually low and depends on the deposition conditions. With the elimination of electron-ion bombardment, the amount of Si-O bond in the films increases, which was recorded by the shift of the absorption peak in the IR spectrum.

Thus, the bombardment with low-energy particles initiates the reaction of the nitride compounds formation on the substrate, and the complete elimination of electron-ion bombardment leads to a violation of stoichiometry towards the formation of oxynitride films. At the same time, intensive bombardment with electrons and ions causes defects to appear in the films, as well as deterioration of the silicon-nitride interface.

4. Changes in the properties of complex films under plasma interaction conditions

The obtained information on the effect of gas discharge plasma on the formation of complex films was used in the development and adaptation of the technology of deposition of low-resistance optically transparent films of indium oxide doped with tin \( \text{In}_{2-y} \text{Sn}_y \text{O}_{3-2y} \) (indium tin oxide, ITO) on a LED heterostructures’ surface [15]. The technology of ITO films deposition developed by us earlier allows to obtain films with controlled values of specific surface resistance from \((5–10) \Omega \cdot \text{m}^2\) to \((2–4) \text{MOhm} \cdot \text{m}^2\) with transparency level of 85% [16].

The minimum surface resistance was obtained while depositing the ITO films by reactive magnetron sputtering of a metal target made of indium alloy (90%) and tin (10%) in an oxygen-containing atmosphere with a partial oxygen pressure of 0.018 Pa and subsequent annealing in vacuum immediately after sputtering for 30 minutes at a temperature of 250 °C without the unwarming of the working chamber. After such high-temperature annealing, the surface resistance of the films was less than \(10 \Omega \cdot \text{m}^2\) [17].

When introducing the developed functional thin-film layers forming technologies into the technological route in the optoelectronic devices production, a need to adapt the ITO film deposition process arose, to obtain coatings by the ion-plasma method on the surface of heteroepitaxial structures of optoelectronic devices. The need is caused by the fact that when coating is applied by magnetron sputtering, the heteroepitaxial structure of the device is subjected to considerable bombardment with high-energy charged particles, which causes radiation defects and nitrogen vacancies that are donors in GaN, and that, of course, leads to its degradation [4, 5].

In order to reduce the negative effect of plasma on heterostructures, an additional device was developed for the magnetron sputtering system, which rejects charged high-energy electrons from the substrate and the growing film during ion-plasma deposition and thereby prevents electron-ion bombardment of the substrate [18].

The magnetic system which deflects high-energy electrons passing through it has a shape of a rectangular steel case with permanent magnets attached to it on two opposite sides, so that the magnetic field created by them in the internal part of the system is directed orthogonally to the atoms of the sputtered target deposited on the substrate.

To track the efficiency of charged particles removal from the substrate by the developed magnetic deflection system with a single Langmuir probe located near the substrate, the probe’s IV characteristic was measured and used to calculate the electron concentration and energy [19]. The measured data showed that the introduction of a magnetic deflecting system made it possible to reduce the energy of electrons by five times, and the concentration of electrons reaching the substrate by more than 13 times.

As a result of the application of the magnetic deflecting system during the deposition of ITO films on the surface of the p-GaN layer of the AlGaN heteroepitaxial structure, the electron energy was reduced five times, and the plasma concentration at the surface of the heteroepitaxial structure decreased...
by more than one and a half orders of magnitude. However, the decrease in the influence of the gas discharge plasma on the growing film caused a drastic increase in the resistance of the deposited ITO films. When studying the surface of the obtained films, it was observed that films with low surface resistance obtained without removing the plasma from the substrate have a smooth homogeneous structure (figure 3a), while pronounced cracks were found on films deposited using the magnetic deflector system (figure 3b), which being defects of the films undoubtedly contribute to an increase in their surface resistance.

Figure 3. The surfaces of the obtained samples of ITO films.

The cracking of the film during its deposition with the diverting system is due to the fact that by withdrawing the high-energy electrons from the substrate that heated it, the substrate temperature was significantly reduced during the deposition (approximately 100–150 °C). As a result, strong mechanical stresses arise in the growing film.

Eliminating this phenomenon allowed the substrate to be heated directly during spraying with an individual heater. For this, a photonic heater with halogen lamps with a total power of 200 watts as the heating element was manufactured. The heater made it possible to maintain the substrate temperature during sputtering at the level of 200–250 °C, which is required to obtain large crystallites in ITO film [5]. With such temperature maintenance, the growth of the film without the defects formation occurs which made it possible to restore their surface resistance to the initial one.

The study of the phase composition by X-ray phase analysis of samples of the ITO films deposited without using the proposed magnetic deflection system and using it showed that, immediately after the application of the ion-plasma method, ITO films have amorphous structure. In the process of ITO films (sprayed with or without a magnetic deflecting system) annealing the partial formation of a crystalline structure in the bulk of the film occurs equally. However, the bulk of the film continues to be in the amorphous phase. At the same time, the orientation of the reflection planes (222) prevails and corresponds to a closely packed plane [111] where the most intensive crystal growth occurs in its direction (figure 4).

In the temperature range from −180 °C to +20 °C, the analysis of the studied samples electrical conductivity temperature dependencies showed the identity of the electrical conductivity schemes and their correspondence to the metallic type of conductivity. At the same time, the average value of the resistance temperature coefficient was $3.5 \times 10^{-4}$ degrees$^{-1}$. Such a value in its order corresponds to the resistance temperature coefficient for metals and is due to scattering by phonons, defects, and impurity ions.
5. Conclusion
Thereby, it was established that, during ion-plasma sputtering of metal targets in the medium of active gases, the formation of final compounds (Si$_3$N$_4$, AlN, Al$_2$O$_3$, In$_2$O$_3$: Sn) occurs right on the substrate, with atoms and metal ions, as well as gas molecules and ions of the working atmosphere, arriving.

It was also established that even at low discharge power the substrate temperature significantly increases in the process of complex thin films deposition by ion-plasma methods. At the same time, the direct heating of the substrate, that forms stoichiometric complex films, plays the most important role in contribution to the crystalline phase formation. However, the plasma effect is manifested not only in the heating of the substrate surface, but also in the appearance of a negative potential on it.

Thus, the formation of films by ion-plasma methods is accompanied on the one hand by the negative impact of electron-ion bombardment on a substrate with a growing film, and on the other hand, by low-energy electron-ion bombardment that contributes to the formation of stoichiometric films.

Acknowledgments
This work was supported by RFBR according to the research project No. 18-32-00708.

References
[1] Aderhold J, Davydov V Yu, Fedler F et al 2001 J. Cryst. Growth 222 701
[2] Ham M and Lou K A 1990 J. Vac. Sci. Technol. A 8 2143
[3] Velikovsky L E, Krasovitsky D M, Mokerov V G et al 2001 Abstracts of the All-Russian Conference "Nitrdes of gallium, indium and aluminum - structures and devices" p 47
[4] Bitner L R, Vedernikov V A, Danilina T I and Manyakhina G V 1976 Russian Physics Journal 19 11
[5] Smirnova I P, Markov L K, Pavlyuchenko A S, Kukushkin M V and Pavlov S I 2014 Semiconductor Physics and Technology 48 61
[6] Markov L K, Smirnova I P, Pavlyuchenko A S, Arakcheeva E M and Kulagina M M 2009 Semiconductor Physics and Technology 43 1564
[7] Danilina T I, Troyan P E, Sakharov Yu V and Zhidik Yu S 2017 Reports of Tomsk State University of Control Systems and Radioelectronics 20 40
[8] Bitner L P and Danilina T I 1979 Microelectronics 1 p17
[9] Volpias V A, Tumarkin A V, Mikhailov A K, Kozyrev A B and Platonov R A 2016 Tech. Phys. Lett. 42 87
[10] Gabovich M D 1972 Physics and technology of plasma ion sources (Moscow: Atomizdat) p 304
[11] Krylov P N, Zakirova P M, Fedotova I V and Gilmudtinov F Z 2013 Physics and technology of semiconductors 47 859
[12] Bitner L R 2007 Vacuum and plasma electronics (Tomsk: Tomsk University of Control Systems and Radioelectronics Publishing) p 148
[13] Hu S M, Kerr D K and Gregor L V 1967 *Appl. Phys. Lett.* **10** 97
[14] Vorobiev G A, Danilina T I, Krivoschekov V P, Smirnova K I and Shandra Z A 1972 *Izv. USSR Academy of Sciences, inorganic materials* **10** 3
[15] Zhidik Y S and Troyan P E 2012 *Reports of Tomsk State University of Control Systems and Radioelectronics* **26** 169
[16] Zhidik Yu S, Troyan P E and Sakharov Yu S 2014 *Reports of Tomsk State University of Control Systems and Radioelectronics* **31** 99
[17] Saharov Yu V, Troyan P E and Zhidik Yu S *Reports of Tomsk State University of Control Systems and Radioelectronics* **37** 85
[18] Troyan P E, Gumerova G I and Zhydik Yu S 2016 *Patent of the Russian Federation for invention* 2601903
[19] Zhidik Yu S and Troyan P E 2014 *Reports of Tomsk State University of Control Systems and Radioelectronics* **34** 52