POLİTEKNİK DERGİSİ

JOURNAL of POLYTECHNIC

ISSN: 1302-0900 (PRINT), ISSN: 2147-9429 (ONLINE)
URL: http://dergipark.org.tr/politeknik

Method for low-temperature vacuum-thermal cleaning of surface single crystals Si and GaAs

Yüzey Si ve GaAs tek kristallerinin düşük sıcaklıklı vakum-termal temizliği yöntemi

***Yazar(lar) (Author(s))**: Z.A. TURSUNMETOVA[1], G.T. IMANOVA[2], I.R. BEKPULATOV[3]*

ORCID[1]: 0000-0002-6512-6739

ORCID[2]: 0000-0003-3275-300X

ORCID[3]: 0000-0001-6311-6631

To cite to this article: Tursunmetova Z.A., Imanova G.T., Bekpulatov I.R., "Method for low-temperature vacuum-thermal cleanıng of surface sıngle crystals Si and GaAs", ***Journal of Polytechnic***, 26(4): 1441-1444, (2023).

Bu makaleye şu şekilde atıfta bulunabilirsiniz: Tursunmetova Z.A., Imanova G.T., Bekpulatov I.R., "Yüzey Si ve GaAs tek kristallerinin düşük sıcaklıklı vakum-termal temizliği yöntemi", ***Politeknik Dergisi***, 26(4): 1441-1444, (2023).

Erişim linki (To link to this article): http://dergipark.org.tr/politeknik/archive

DOI: **10.2339/politeknik.1119884**

Method For Low-Temperature Vacuum-Thermal Cleaning of Surface Single Crystals Si and GaAs

Highlights

- *Si(111) and GaAs(111) films are a narrow-gap semiconductor with a band gap of 0.7 eV and have good emission and thermoelectric properties corresponding to the solar spectrum.*
- *Si(111) and GaAs(111) films have high photoelectric and thermoelectric characteristics.*

Graphical Abstract

Surface composition studies using AES revealed that in the near-surface region of GaAs there are impurities such as O, C, S, P, N, and Si - O, C, S, Na, N.

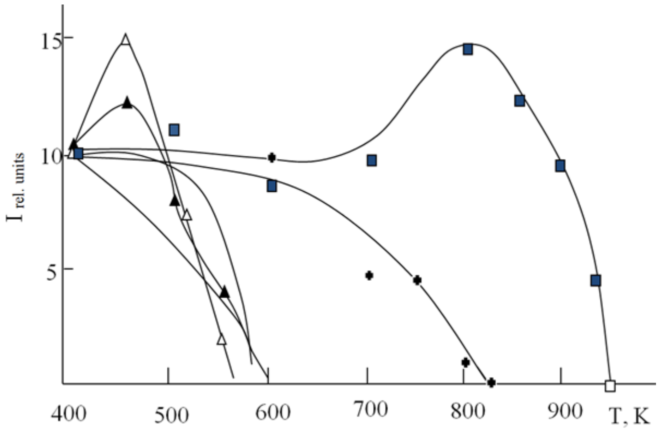

Figure. Dependences of the intensity of lines of Auger electrons of a number of impurity atoms present on the surface of gallium arsenide on the heating temperature in vacuum

Aim

The paper reports on a method of low-temperature vacuum-thermal cleaning of the surface of Si and GaAs single crystals developed by the authors, which consists in implanting Ba+ ions (or alkaline elements) into Si and GaAs crystals preliminarily cleaned by ultra-high.

Design & Methodology

Auger electron spectroscopy (AES), elastically scattered electron spectroscopy (ESES), photoelectron spectroscopy (PES) and slow electron diffraction (LEED) methods was used in this study.

Originality

The study good emission and thermoelectric properties corresponding to the solar spectrum and have high photoelectric and thermoelectric characteristics determination.

Findings

Si band gap upon implantation of large doses of GaAs also contributes to defects formed as a result of strong disordering of the crystal lattice.

Conclusion

In this work, Si(111) and GaAs(111) films are a narrow-gap semiconductor with a band gap of 0.7 eV respectively.

Declaration of Ethical Standards

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Politeknik Dergisi, 2023; 26(4) : 1441-1444　　*Journal of Polytechnic, 2023; 26(4): 1441-1444*

Yüzey Si ve GaAs Tek Kristallerinin Düşük Sıcaklıklı Vakum-Termal Temizliği Yöntemi

Araştırma Makalesi / Research Article

Z.A. TURSUNMETOVA[1], G.T. IMANOVA[2*], I.R. BEKPULATOV[3]
[1]Research Institute of Semiconductor Physics and Microelectronics at the National University of Uzbekistan named after Mirzo Ulugbek Tashkent, Uzbekistan.
[*2]Institute of Radiation Problems, Azerbaijan National Academy of Sciences,
AZ 1143 - Baku, Azerbaijan
[3]Tashkent State Technical University, Tashkent, Uzbekistan

(Geliş/Received : 22.05.2022 ; Kabul/Accepted : 15.08.2022 ; Erken Görünüm/Early View : 06.09.2022)

ÖZ

Makale, yazarlar tarafından geliştirilen, Si ve GaAs tek kristallerinin yüzeyinin düşük sıcaklıkta vakum-termal temizleme yöntemi hakkında rapor veriyor, bu, Ba^+ iyonlarının (ve ya alkali elementlerin) Si ve GaAs kristallerine önceden ultra yüksek ile temizlenmiş implantasyonundan oluşuyor. İyon aşındırma ve ardından 800 K - 15 dakika ve 1000 K'de 30 dakika olmak üzere iki aşamalı tavlama ile vakum edilmişdir. Etkin temizlemenin etkisi, aktif olan Ba^+ ve alkali elementlerin iyonlarının ilk aşamada safsızlık atomları (O, C, S, N vb.) ısıtmanın ikinci aşamasından sonra kirliliklerdir.

Anahtar Kelimeler: Tek kristal, yüzey, ultra yüksek vakum, temizleme, implantasyon, alma katmanı.

Method for Low-Temperature Vacuum-Thermal Cleaning of Surface Single Crystals Si and GaAs

ABSTRACT

The paper reports on a method of low-temperature vacuum-thermal cleaning of the surface of Si and GaAs single crystals developed by the authors, which consists in implanting Ba^+ ions (or alkaline elements) into Si and GaAs crystals preliminarily cleaned by ultra-high vacuum by ion etching and subsequent annealing in two stage at 800 K - 15 minutes and at 1000 K for 30 minutes. The effect of effective cleaning is achieved due to the fact that the introduced ions of Ba^+ and alkaline elements, being active, form compounds with impurity atoms (O, C, S, N, etc.) at the first stage and are removed together with impurities after the second stage of heating.

Keywords: Single crystal, surface, ultrahigh vacuum, cleaning, implantation, gettering layer.

1. INTRODUCTION

Interfaces and surfaces are where the action happens. Catalysis, molecular recognition, charge transfer, polymerization and many other critical processes take place at the boundary between one medium and another. With the need to integrate new materials into devices, and applications ranging from catalysis to sensors, medicine to self-cleaning surfaces, and displays to lasers, fundamental and applied studies of surface and interface processes and optimization are of critical importance in developing new technology to meet today's challenges.

Obtaining clean surface of gallium arsenide is an urgent problem of electronic instrumentation, as well as the results of experimental research and various technological operations carried out to create device elements based on Si and GaAs largely depend on the state of their initial surface [1].

Crystal surface cleaning is often used by direct indirect (thermal irradiation, electron bombardment, laser annealing) heating at a temperature below the melting point of the sample. The main disadvantage is that thermal annealing leads to a redistribution of compounds in the main part of the sample or even to their stratification on the surface [2].

A simple and effective purification method is sputtering of these ions by bombarding the crystal surface with Ar^+ ions with energies from 0.5 to 5 keV at transition angles of <15°. The disadvantage of the method is that ion bombardment destroys the surface structure [3].

The samples were analysed using X-ray diffraction (XRD) and Energy dispersive spectroscopy (EDS) to study the microstructural and composition changes. The XRD results showed the crystalline structure for the sample before and after irradiation (with gamma irradiation dose 9.7, 48.5 and 97 kGy). Amorphization of the sample began at the gamma irradiation dose of 145.5 kGy. Increase in gamma irradiation

---

**Sorumlu Yazar (Corresponding Author)*
e-posta : gunel_imanova55@mail.ru

dose had an inverse effect on the activation energy and had a directly proportional effect on the lattice volume [13-15].

The effect of preliminary radiation-oxidative treatment on the current density and current–voltage characteristic of metallic zirconium has been studied. The contribution of preliminary radiation-oxidative treatment to the change in the electrophysical characteristics during thermal and radiation–thermal tests in the contact of zirconium with water is revealed [16-17].

The purpose of this work is to develop a new technology for low-temperature vacuum cleaning of the surface of silicon and gallium arsenide.

2. MATERIAL and METHOD

Single crystals of gallium arsenide (GaAs (111)) and silicon (Si(111)) *n* - and *p* - type with a resistivity of 60 Om·m were chosen as objects of study. The technological chamber made it possible to clean the surface of the materials under study by thermal heating, electron bombardment, ion etching, as well as the implantation of Ba^+ ions and alkaline elements with an energy of 0.5-5 keV, with a different dose: from 10^{13} to $2 \cdot 10^{17}$ cm^{-2}. In addition, it was possible to obtain a clean surface by chipping in an ultrahigh vacuum. Implantation of Ba^+ ions, sample heating, study of their composition and parameters of energy bands using AES methods and measuring the intensity of light passing through the sample were carried out in the same device under ultrahigh vacuum conditions ($P = 10^{-7}$ Pa). Si (111) monocrystal of *p*-type with specific resistance $\rho = 3000$ Ω·cm were chosen as the substrate. Cleaning of the initial crystal was carried out by thermal heating in ultrahigh vacuum $P = 10^{-7}$ Pa in two stages: long-term (for 60-120 min.) at a temperature of T = 900 K and short-term (for 30-60 s) at T = 1500 K The Si surface was also cleaned by a new method developed by the authors of this article. The analytical part of the device with an analyzer of the type of a spherical mirror with a retarding field makes it possible to control the state of the surface using Auger electron spectroscopy (AES), elastically scattered electron spectroscopy (ESES), photoelectron spectroscopy (PES) and slow electron diffraction (LEED) at pressure of residual gases is not more than 10^{-7} Pa [4-8].

3. RESULTS AND DISCUSSION

To achieve this goal (figure 1), we compared the spectra of the surface state (composition and crystal structure) of GaAs (111) and Si (111) purified by various methods. Surface composition studies using AES revealed that in the near-surface region of GaAs there are impurities such as O, C, S, P, N, and Si - O, C, S, Na, N. It can be seen that the main impurities are C, O, S. Oxygen and carbon atoms in the form of molecules cover the cleaned crystal surface with a thick adsorption layer.

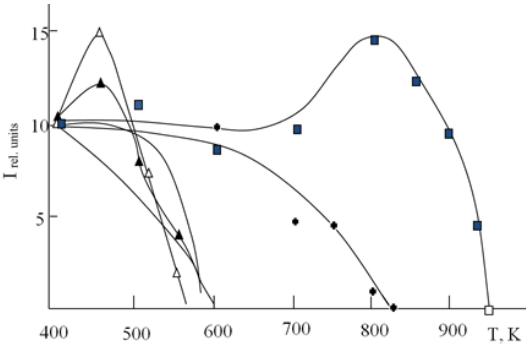

Fig. 1. Dependences of the intensity of lines of Auger electrons of a number of impurity atoms present on the surface of gallium arsenide on the heating temperature in vacuum.

In [9], it is indicated that at a vacuum of 10^{-7} Torr, 1 monolayer of oxygen atoms is adsorbed on the surface of semiconductors in one minute. Temperature ~600 K is sufficient for the desorption of these molecules from the GaAs surface. An increase in the intensity of C starting from 700 K and passing through a maximum at 820 K (curve 1) is associated with the diffusion of carbon atoms from the bulk of the crystal to the surface [10]. The minimum decrease in C intensity can be achieved after annealing at T = 950 K. It is not possible to completely remove O and C by thermal annealing, since heating at higher temperatures leads to partial decomposition of GaAs. Similar dependences of I on T for impurities contained in the near-surface Si region are shown in Fig. 2. As can be seen from the figure, the content of O, C and S on the Si surface during heating from 500 - 600 K increases due to their diffusion from the near-surface region of Si, with a further increase in temperature, their intensities decrease, reaching the minimum values of S at 750 K, O – at 1050 K.

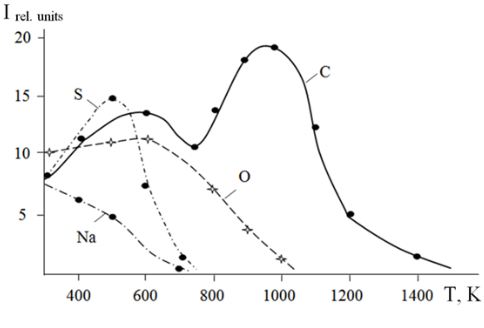

Fig. 2. The dependence of the intensity of the Auger electron lines of a number of impurity atoms present on the silicon surface on the heating temperature.

The appearance of the second maximum at 1000 K for C is probably associated with the onset of diffusion to the surface of bulk carbon, the content of which can be reduced to a minimum only after heating at 1450 K.

Thus, from fig. 1 and 2 that it is not possible to completely remove impurities from Si and GaAs only by thermal heating below the melting temperature of the sample. We set ourselves the task of developing a new method for cleaning the Si(111) and GaAs(111) surfaces.

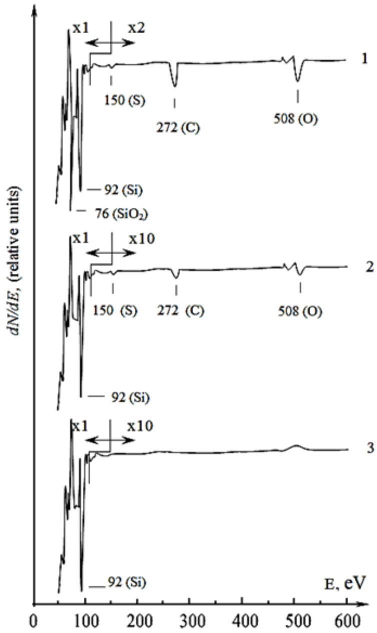

Fig. 3. Auger electron spectra obtained: from the initial Si(111) surface (spectrum 1), from the Si(111) surface cleaned by thermal heating in two stages: for a long time at 1000 K and for a short time at 1500 K (spectrum 2) and from Si(111) surface obtained after thermal heating at T=1500 K Si(111), previously implanted with barium ions with energy E_0=1 keV and radiation dose D=10^{17} cm^{-2} – (spectrum 3).

We solve this problem by creating a getter layer in the near-surface region, previously cleaned by thermal heating of Si(111) and GaAs(111), by implanting Ba^+ (either Rb^+ or Cs^+) ions with an energy of E_0=0.5 – 1 keV and with a high radiation dose 10^{16}-10^{17}sm^{-2} in ultrahigh vacuum at a residual gas pressure of 10^{-7} Pa [10]. The process of impurity gettering becomes most efficient if GaAs is thermally heated at 700 K, and Si at 900 K. At the last stage, we propose to remove the getter layer by ion etching, i.e., by sputtering the surface getter layer with an Ar^+ ion beam with an energy of 1.5 keV, incident at an angle of 15° to the surface [11-12].

Figure 3 shows the spectra of Auger electrons for a silicon surface not subjected to thermal cleaning in vacuum (spectrum 1), after thermal cleaning in a vacuum of 10^{-7} Pa in two stages: long-term (for 1 hour) at T=1000 K and short-term (0.5-1 min) at T=1500 K (spectrum 2) and silicon subjected to purification by our proposed method (spectrum 3). It can be seen that the spectrum of the original silicon before purification has Auger peaks: for silicon oxide SiO_2 at E=76 eV with high intensity; silicon peak $L_{2.3}VV$ at E=92 eV, sulfur peak S at E=150 eV, carbon peak C at E=272 eV, and oxygen peak O at E=508 eV. Conducting thermal cleaning in two stages leads to the disappearance of the oxide film (the peak at 76 eV disappears, spectrum 2), and the intensity of the Auger peaks of S, C, and O impurities decreases by a factor of 10 or more. However, it is not possible to completely clean the Si surface from impurities by thermal heating even at high heating temperatures. Implantation of Ba ions into silicon preliminarily cleaned by thermal heating and subsequent removal of the getter layer by ion etching, as can be seen from spectrum 3, makes it possible to almost completely (within the sensitivity of the Auger spectrometer) clean the Si surface from impurities. A similar cleaning effect was observed by us after such treatment of the GaAs surface. Moreover, by changing the energy of the implanted ions, it is possible to control the depth of the area to be cleaned.

In addition, the study of the crystalline perfection of crystals by the LEED method showed that the LEED pattern taken from the Si(111) surface subjected to cleaning by the method proposed by us is more contrasting (Fig. 4b) than the LEED pattern from the Si(111) surface subjected to thermal cleaning in high vacuum (Fig. 4a), which indicates the best crystalline perfection of the crystal surface obtained by us.

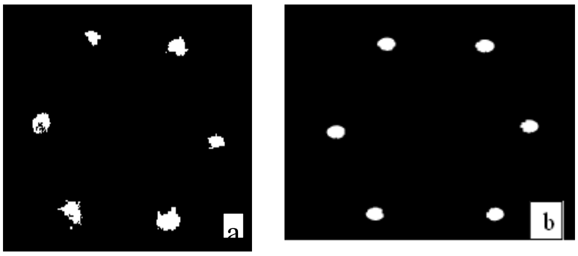

Fig. 4. LEED pictures taken: after purification of Si(111) by thermal heating in two stages – a; after thermal heating at T=1500K Si(111) previously implanted with Ba^+ ions with energy E_0=1 keV and radiation dose D=10^{17}cm^{-2} –b.

The technology we have developed for low-temperature vacuum cleaning of Si and GaAs can be used directly in the process of growing single crystals. It is expected that the application of the proposed technology will improve the quality and yield of suitable device structures based on Si and GaAs, since the performance of devices is largely determined by the degree of purity of the surface region of semiconductor crystals on which the functional elements of devices are formed.

4. CONCLUSION

Thus, the proposed method for low-temperature vacuum-thermal cleaning of the surface of Si and GaAs single crystals, which consists in creating a getter layer by implanting Ba^+ ions (or alkaline elements) with a low energy and a high radiation dose, heating the samples at a temperature of 900 and 700 K, respectively, and in ion etching of the surface layer allows not only to obtain a clean surface of Si(111) and GaAs(111), but also to significantly improve their crystalline perfection. It is shown that Si(111) and GaAs(111) films are a narrow-gap semiconductor with a band gap of 0.7 eV and have good emission and thermoelectric properties corresponding to the solar spectrum and have high photoelectric and thermoelectric characteristics. It should be noted that, in addition to the formation of a chemical compound, the narrowing of the Si band gap upon implantation of large doses of GaAs also contributes to defects formed as a result of strong disordering of the crystal lattice.

DECLARATION OF ETHICAL STANDARDS

The author of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

AUTHORS' CONTRIBUTIONS

Z.A. Tursunmetova: Performed the experiments and analyse the results, wrote the manuscript.

G.T. Imanova: Performed the experiments and analyse the results, wrote the manuscript.

I.R. Bekpulatov: Performed the experiments and analyse the results, wrote the manuscript.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

REFERENCES

[1] Oura, K., Lifshits, V.G., Saranin, A.A., Zotov, A.V., Katayama, M., "Surface Science: An Introduction", ***Spri.Sci. & Busi.Med.***, 440: (2013).

[2] Malysheva, I.A., "Technology of production of microelectronic devices", ***M: Ener.,*** 74-75, (1980).

[3] Roth, A., "Vacuum technology", ***Amster. Elsev***., 554: (1990).

[4] Norichika, Y., Takehiko, S., Minoru, M., Pat. USA 2007/0077191A1 Pub. Date: Apr. 5, (2007).

[5] Konov, V.I., Pimenov, S.M., Prokhorov, A.M., Chapliev, N.I., ***Russ., Sur.Phy.Chem.Mech.,*** 12: 1-98, (1987).

[6] Nemtsev, G.Z., Pekarev, A.I., Chistyakov, Yu.D., ***Microelec.,*** 12(5): 432-439, (1983).

[7] Rysbaev, A.S., "Changes in the secondary-emission properties of the Si surface during ion implantation and subsequent annealing", ***Rad. Engine. and elect.,*** 46(7):. 883-885, (2001).

[8] Normuradov, M.T., Rumi, D.S., Rysbaev, A.S., Izv. "Academy of Sciences of the Uzbek SSR". ***Ser. Phys-Math.,*** 4: 70-73, (1986).

[9] Dobretsov, L.N., Gomoyunova, M.V., "Emission electronics", ***M.:Nau.,*** 1-408, (1966).

[10] Utamuradova, Sh.B., Tursunmetova, Z.A., Nasriddinov, S.S., Abraeva, S.T., ***Abstracts of the 50th International Tulinov Conference on the Physics of the Interaction of Charged Particles with Crystals***, 1-145, (2020).

[11] Risbaev, A.S., Khujaniyazov, J.B., Bekpulatov, I.R., Rakhimov, A.M., ***J.of Surf.Inv.: X-ray., Synchrotron and Neutron Techniques,*** 11(5): 994–999, (2017).

[12] Imanova, G., Bekpulatov, I. "Investigation on the Electronic Structure of Nanosized Barium Monosilicide Films Produced by Low-energy Implantation of Ba^+ Ions in Si", ***Amer. Jou. Of Nan. Rese. and Appli.,*** 9(4): 32-35, (2021).

[13] Kozlenko, D.P., Dang, N.T., Jabarov S.H., "Pressure-induced modifications of the magnetic order in the spin-chain compound $Ca_3Co_2O_6$", ***Phys. Rev. B***, 98, 134435, (2018).

[14] Mirzayev, M.N., Jabarov, S.H., "X-ray diffraction and thermodynamics kinetics of SiB6 under gamma irradiation dose", ***Silicon***, 11: 2499–2504, (2019).

[15] Mirzayev, M.N., "Influence of gamma irradiation on the surface morphology, XRD and thermophysical properties of silicide hexoboride", ***Mod. Phy. Lett. B,*** 32(14): 1850151, (2018).

[16] Agayev, T., Imanova. G., Aliyev A., "Influence of gamma radiation on current density and volt–ampere characteristics of metallic zirconium", ***Inter. Jour. of Mod. Phy. B,*** 36(19): 2250115, (2022).

[17] Imanova, G.T.. Agayev, T.N., Jabarov, S.H., "Investigation of structural and optical properties of zirconia dioxide nanoparticles by radiation and thermal methods", ***Mod. Phy. Lett. B,*** 35(02): 2150050, (2021)