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Study of The Process of Formation of Heterostructural Nanofilms Me_xSi_y/Si and Ga_xMe_{1-x}As/GaAs by Ion Implantation

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ABSTRACT: *This study explores the formation of thin heteroepitaxial multi-component films (with a thickness of $d \leq 100$ nm) on the surfaces of autoepitaxial silicon (Si) and gallium arsenide (GaAs) through the processes of ion implantation and subsequent annealing. Ion implantation involves introducing active elements into the material, which can significantly alter its properties. The research identifies the types of compounds formed during this process and examines the energy band parameters of the resulting films. It was discovered that when low-energy ions of active metals are implanted, the surface of GaAs becomes completely amorphous at a dose greater than $(4–8)\cdot10^{16}$ sm^{-2}. Additionally, recrystallisation during laser annealing initiates at energy densities between (0.7 to 0.8) J·sm^{-2}. These findings are crucial for advancing semiconductor technologies, as they provide insights into how the structural and electronic properties of semiconductor materials can be manipulated. Understanding these processes opens new avenues for developing more efficient electronic and optoelectronic devices, which are essential for modern technology. Overall, this work contributes to the field of materials science by enhancing our knowledge of thin film formation and properties.*

Keywords: ion implantation, annealing, thin heteroepitaxial multi-component films, surface amorphisation, recrystallisation

1. INTRODUCTION

One of the modern methods for obtaining multilayer heteroepitaxial films is the ion implantation method. Recent studies have provided insights into the formation of chemical bonds, surface disordering and changes in the valence electron density of states for various materials implanted with active elements.[1–6] The electronic properties of barium silicide (BaSi), barium disilicide ($BaSi_2$), sodium disilicide ($NaSi_2$) and gallium-barium arsenide ($Ga_{1-x}Ba_xAs$) obtained by ion implantation and annealing have also been investigated, indicating the formation of narrow-gap semiconductor properties.[5] However, more systematic studies using advanced surface diagnostics are needed to fully understand the changes in electronic state, atomic structure and phase formation mechanisms, particularly in the case of gallium arsenide (GaAs).[7–14]

There is a lot of scientific literature on the search for materials with metal-semiconductor properties. Thin gallium indium phosphide (GaInP) films were grown on the gallium phosphide (GaP) surface using molecular beam epitaxy and ion implantation procedures. In the work of Shirinov et al., the energy and angular dependences of the secondary electron emission coefficient of GaInP films were also studied by Auger electron spectroscopy (AES), ultraviolet photoelectron spectroscopy (UPS), light absorption and the analysis of experimental data made it possible to determine for the first time the main energy bandgap and emission parameters of the $Ga_{0.6}In_{0.4}P$/GaP(111) nanofilm. The bandgap width was found to be 1.85 eV, which was significantly smaller than the width of the GaP substrate, so the maximum value of the SEEC s_{max} and the quantum yield of photoelectrons K (at $h\upsilon = 10.8$ eV) values. The $Ga_{0.6}In_{0.4}P$/GaP system was slightly reduced compared to pure GaP.[15] However, the effects of thermal heating and laser heating after ion implantation are largely unstudied. In this work, we have obtained heterostructural films on the surface of monocrystalline auto-epitaxial silicon films (p-type, $N_B = 10^{18}$ sm^{-3}; n-type, $N_P = 10^{16} sm^{-3}$) and GaAs (p-type, $N_{Zn} = 10^{19}$ sm^{-3}) using the ion implantation method. The thickness of these films is 500 Å–1000 Å.

2. RESEARCH METHODS

The technological processing of the films (ion implantation, thermal and laser annealing) and the study of their composition and electronic state were carried out in the same universal experimental device under conditions of ultra-high vacuum ($P = 10^{-8}$ Pa). The elemental and chemical composition of the studied films was determined by AES, and the electronic structure of the surface was studied by UPS. The depth profiles of the atomic distribution were studied by AES combined with ion sputtering. Ar^+ ions with $E_0 = 3$ keV were used. Sputtering was carried out at an angle of incidence of ~85° relative to the normal. The degree of disordering of the GaAs surface during ion implantation and its recrystallisation during annealing, the type and parameters of the lattice were studied by the method of reflection high-energy electron diffraction (RHEED), the diffraction patterns were recorded on a standard EMR-2 setup. The experimental technique is described in detail in.[5]

In previous work, it was shown that by using low-energy ion implantation combined with annealing, it is possible to obtain thin multi-component films of the types BaSi, $BaSi_2$, $NaSi_2$ and $Ga_xBa_{1-x}As$ in the near-surface region of Si and GaAs bulk crystals.[16] These films had a predominantly crystalline lattice similar to the matrix, but the parameters of their lattices differed significantly (up to 10%–15%) from each other.

Implantation was carried out using barium $(Ba)^+$, strontium $(Sr)^+$ and sodium $(Na)^+$ ions with an energy E_0 = 0.5 keV–5 keV and a fluence of D = 10^{14} sm^{-2}–10^{17} sm^{-2}. Annealing was performed by high-temperature heating or pulsed laser irradiation (λ = 0.53 μm, pulse duration 10 ns). Uniform multi-component films were obtained by combining ion implantation and laser annealing. Additionally, a brief high-temperature annealing step after laser irradiation was required to improve the perfection of the crystalline lattice. These films had a specific composition that depended on the type of doping ions. For example, in the case of Ba ion implantation, the most stable and homogeneous epitaxial films had the following composition: $BaSi_2$, $Ga_{0,6}Ba_{0,4}As$ (the brief annealing was carried out 10–15 times at an allowable high temperature T_{max} for 30 s–40 s). A transition layer was formed between the heterostructure and the original film.

3. RESULTS AND DISCUSSION

Table 1 presents the optimal conditions for obtaining heterostructure films for Si and GaAs films deposited with Ba ions. At low ion energies, very thin (d = 30 Å–40 Å) films were obtained. At higher energies ($E_0 \geq 3$ keV), the uniformity of the films deteriorated significantly. This is because recrystallisation processes may have occurred in the ionised film, which would have improved the film quality. Higher energy leads to deeper penetration of ions into the material, which increases the film thickness. Therefore, in order to obtain relatively thicker and uniform films, the ion energy was changed from 5 keV to 1 keV. The ion dose in all cases was close to the saturation dose, which was in the range of $(1–6)\cdot10^{16}$ sm^{-2}.

Table 1: Optimal conditions for ion implantation and annealing to obtain heterostructure films based on Si and GaAs.

The original film	Ion implantation		Annealing		Film composition	Thickness of films (Å)	Thickness of the transition layer (Å)
	E_0 (keV)	D (sm^{-2})	W ($J.sm^{-2}$)	$T_{мах}$ (K)			
Si	0.5	2.10^{16}	1.5	1,100	$BaSi_2$	30–40	40–50
Si	1	4.10^{16}	1.5	1,400	$BaSi_2$	40–50	40–50
Si	5–1	6.10^{16}	1.8	1,500	$BaSi_2$	80–100	60–80
GaAs	1	2.10^{16}	1.2	900	$Ga_{0,6}Ba_{0,4}As$	30–40	40–50
GaAs	5–1	6.10^{16}	1.5	1,000	$Ga_{0,6}Ba_{0,4}As$	100–180	80–100

Changing the ion dose also changes the concentration gradients in the film, which affects the physical and chemical properties of the ionised film. Increasing the ion energy $E_0 > 5$ keV led to a decrease in the concentration of doping ions in the region of maximum scattering and an increase in the surface scattering coefficient. In a similar way, epitaxial films of $SrSi_2$, $Ga_{0.5}Sr_{0.5}As$, NaSi and $Ga_{0.4}Na_{0.6}$. As were obtained, Figure 1 shows the depth profiles of Na atoms in GaAs implanted with Na^+ ions at $E_0 = 1$ keV and $D = 4 \cdot 10^{16}$ sm^{-2}. The depth profile of Na atoms in GaAs implanted with Na^+ ions at an energy of 1,000 eV and a dose of $4 \cdot 10^{16}$ sm^{-2} shows a decrease in the concentration of Na^+ atoms as expected after heating at 900 K for 30 min, and it is linear. We can see that the change in the depth profile after laser heating at a power of $W = 1.2$ $J \cdot sm^2$ at 900 K is relatively small, but the depth is the same as before. This means that laser heating is more effective. It can be seen that after such annealing, the concentration of Na atoms (and consequently Ga and As) remains almost unchanged to a depth of 40 Å–50 Å, i.e., a sufficiently homogeneous $Ga_{0,4}Na_{0,6}As$ -type layer is formed.

Figure 2 shows high-energy electron diffraction patterns for GaAs implanted with Ba^+ ions. RHEED patterns for GaAs implanted with Ba^+ ions at an energy of $E_0 = 500$ eV and a dose of $D = 4 \cdot 10^{16}$ sm^{-2} show that the GaAs is low amorphous when heated to 700 K in Figure 2(a). In Figure 2(b), amorphous ion film patterns were observed as a result of laser heating at 700 K. The electron diffraction pattern of the ion film heated at 1,000 K (see Figure 2[c]) shows a diffuse ring - an amorphous halo, which indicates the amorphisation of the GaAs near the surface layer.

After several cycles of short high-temperature heating, parallel lines characteristic of single-crystal films appears in the electron diffraction pattern. Using these electron diffraction patterns, we estimated the type and parameters of the lattice. In our case, epitaxial films with a cubic lattice were always formed if the thickness of the resulting films did not exceed 100 Å–150 Å. Table 2 shows the lattice constant values of the multicomponent films obtained as a result of ion implantation combined with annealing (laser + T_{max}). Differences in the lattice constants of the multicomponent films of the silicide/Si interface obtained as a result of ion implantation combined with annealing directly affect the mechanical stress and heterostructure integration.

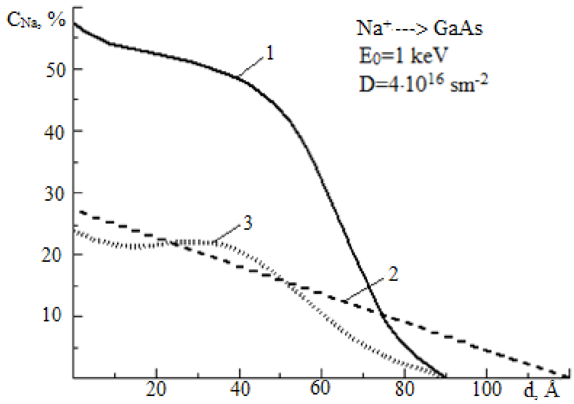

Figure 1: Effect of annealing on the depth profiles of Na atoms.

Note: 1 = after ion implantation; 2 = after thermal annealing at T = 900 K for 30 min; 3 = after laser annealing (at W = 1.2 J·sm^2) and rapid thermal annealing (T=900 K).

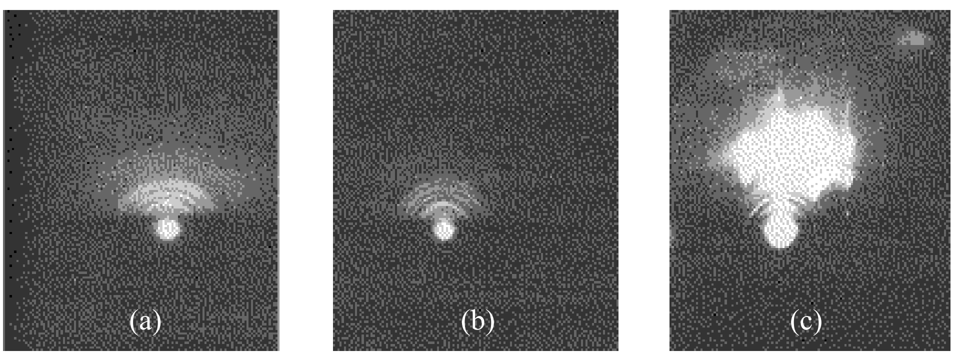

Figure 2: RHEED patterns of GaAs doped with Ba^+ ions at E_0 = 0.5 keV (D = 6·10^{16} sm^{-2}), obtained after annealing at the following temperatures.

Note: (T) = (a) 700 K; (b) 800K; (c) 1,000K.

These stresses can reduce the quality of the interface and worsen the properties of the materials. Therefore, it is important to control and optimise these processes. As can be seen from Table 2, the lattice constants of silicide films differ significantly from the lattice constants of pure silicon films. This, in turn, can lead to the appearance of significant mechanical stresses at the silicide/silicon interface. To reduce mechanical stress, it is necessary to create high-quality interfaces between the silicide/Si materials. This reduces stress and improves electrical properties. The fact that the lattice constant of silicide's is larger than that of silicon indicates that there is a strain between these materials. However, as shown below, due to the presence of a transition layer at this interface, the strain between the layers is sharply reduced. The lattice constants of the ternary systems formed in GaAs and the matrices differ little from each other.

Table 2: The lattice constant values for the Me_xSi_y and $Me_xGa_{1-x}As$ systems.

In the present work		In the literature	
Film structure	a (Å)	a (Å)	Literature
Si	5.4	5.43	17
$BaSi_2$	6.45±0.1	6.715	–
		6.54	18
NaSi	6.85	8.9	6
		6.545	–
$SrSi_2$	5.9	–	–
GaAs	5.7	5.63	19
$Ga_{0.6}Ba_{0.4}As$	5.8	–	–

To obtain information about the electronic structure of the surface of the created films, the UPS method was used. As an example, Figure 3 shows the photoelectron spectra of GaAs and $Ga_{0,6}Ba_{0,4}As$. These spectra reflect the form of the distribution of the density of electronic states in the valence band.[20] It can be seen that the density of valence electron states in GaAs and Ga-Ba-As differ significantly from each other. Similar results were obtained for silicide films and other ternary compounds created in the near-surface region of GaAs. Based on the analysis of the photoelectron spectra, we have determined the main macroscopic parameters of the energy bands of the studied films (see Table 3).

Table 3: The parameters of the energy bands for the studied systems.

The studied structure	The main energy parameters, in eV				
	E_V	E_F	E_g	χ	V_S
Si (100)	5.1	4.7	1.1	4.0	0.3
$BaSi_2$	4.0	3.9	0.7	3.3	–
GaAs, p-type,	5.2	5.0	1.4	3.8	0.1
$Ga_{0,6}Na_{0,4}As$	5.3	5.2	1.7	3.6	–

From Table 3, it can be seen that the positions of the valence band top E_V and the Fermi level E_F in the case of pure silicon differ significantly (~0.4 eV), which is not typical for p-type semiconductors. This difference is due to the occurrence of a significant band bending V_S on the surface. In the case of GaAs, the magnitude of the bending and, accordingly, the difference in the values of E_V–E_F is small.

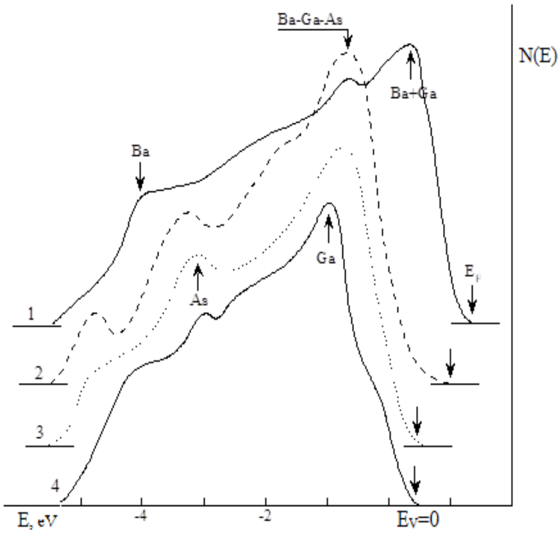

Figure 3: The influence of thermal annealing on the PES (photoelectron spectroscopy) of Ba-doped GaAs with E_0 = 0.5 keV at T : 1 = 300 K; 2 = 800; 3 = 900 K; 4 = 1,000 K.

In the case of $BaSi_2$ and $Ga_{0,6}Na_{0,4}As$, the surface band bending is practically (within the sensitivity of the photoelectron spectrometer ~1%) not observed. When transitioning from Si to $BaSi_2$, the bandgap E_g decreases sharply. The partial replacement of Si atoms with metal atoms and the formation of metal silicides always leads to a decrease in the bandgap width.[19,20]

In contrast to the silicide, $Ga_{0,6}Na_{0,4}As$ has a relatively large bandgap compared to GaAs. Our estimates have shown that the bond between Na and As atoms has an ionic-covalent character. Apparently, an increase in the degree of ionicity of the bond is one of the main reasons for the increase in the dielectric properties of GaAs. Note that $Ga_{0,6}Me_{0,4}As$ films with a large E_g (bandgap) were obtained by us only under certain annealing conditions: W = 1.2 J·sm^{-2} and T_{max} = 1200 K. In other cases, for example, after laser annealing, the E_g value of the system was within 0.7 eV–0.8 eV. In previous work, it was shown that the bandgap width of the Ga-Me-As system created on the surface of bulk GaAs is significantly smaller (0.6 eV–0.8 eV) than for pure GaAs.[6] This effect is apparently associated with the presence of various types of crystal structure defects and the formation of a large number of levels near the valence band top and the conduction band bottom.

4. CONCLUSIONS

In this work, the physical properties of the silicide/Si interface were studied as a result of ion implantation of the Si surface using Ba^+, Sr^+ and Na^+ ions with an implantation energy of $E_o = 500$ eV–5,000 eV and a dose of $D = 10^{14}$ sm^{-2}–10^{17} sm^{-2}. The formation of thin ($d \leq 100$ Å) heteroepitaxial nanolattices in the near-surface region of auto epitaxial Si and GaAs films during the implantation process of active element ions in combination with annealing after implantation and heating as a result of laser heating was shown. The depth profiles of the atomic distribution were studied by AES in combination with ion scattering. After laser annealing, the concentration of Na atoms (and therefore Ga and As) practically does not change at a depth of 40 Å–50 Å, i.e., a sufficiently homogeneous $Ga_{0.4}Na_{0.6}As$-type layer is formed. It was found that when implanting low-energy ions of active metals, the complete amorphisation of the GaAs surface occurs at $D > 8 \cdot 10^{16}$ sm^{-2}, and during laser annealing, recrystallisation begins at $W = 0.7$ $J \cdot sm^{-2}$. We believe that this study will serve to develop scientific research on improving the physical properties of heteroepitaxial thin films formed as a result of laser heating after ion implantation.

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