ISSN: 2181-3906
2024

International scientific journal
«MODERN SCIENCE AND RESEARCH»
VOLUME 3 / ISSUE 2 / UIF:8.2 / MODERNSCIENCE.UZ

ELECTRONIC SPECTROSCOPY OF HETEROSYSTEM SI/CU SURFACES WITH NANOSCALE PHASES AND FILMS

A.A. Mustafoev
Jizzakh Polytechnic Institute.
E-mail: ***abduvohid030898@gmail.com***

https://doi.org/10.5281/zenodo.10629056

Abstract. *In this article, valence electron state density, energy band parameters, energetic, optical and electrophysical properties of metal oxide and silicide films with thickness ≤ 40 Å formed on Si/Cu surface during ion implantation and annealing were studied.*

Key words: *thermal oxidation, nanophases, nanofilms, plasma oscillation, surface roughness, optical-phonon mode, island growth.*

ЭЛЕКТРОННАЯ СПЕКТРОСКОПИЯ ПОВЕРХНОСТЕЙ ГЕТЕРОСИСТЕМ SI/CU С НАНОРАЗМЕРНЫМИ ФАЗАМИ И ПЛЕНКАМИ

Аннотация. *В статье исследованы плотность состояний валентных электронов, параметры энергетических зон, энергетические, оптические и электрофизические свойства пленок оксидов металлов и силицидов толщиной ≤ 40 Å, образующихся на поверхности Si/Cu в процессе ионной имплантации и отжига.*

Ключевые слова: *термическое окисление, нанофазы, нанопленки, плазменные колебания, шероховатость поверхности, оптико-фононный режим, рост островков.*

Introduction

Recently, nanoscale structures obtained on the surface and near it for materials of various natures have been widely studied, which is due to their promise for the development of new POP and MIS structures for solid-state electronics devices. Nanoscale systems can be obtained using molecular beam, solid-phase and gas-phase epitaxy and ion bombardment methods. In this case, it is of particular interest to obtain and study the properties of nanostructures based on freely hanging films. Previously, the patterns of formation of nanosized films of SiO_2 and MeS_{i2} (Me is a metal) on the surface of a thin free-hanging Si/Cu heterostructure were studied. In particular, it was found that the SiO_2 film obtained by ion bombardment followed by heating contains a large amount of non-stoichiometric SiO_x oxides and unbound Si atoms (5–6 at.%), and the BaSi2 and $CoSi_2$ films contain excess metal atoms - up to 10 at. %. In this case, the Eg of the SiO_2 and $BaSi_2$ films decreased by more than two times [1-2].

In this dissertation, the densities of state of valence electrons, energy band parameters, energetic, optical and electrophysical properties of metal oxide and silicide films with a thickness of ≤ 40 Å formed on the Si/Cu surface during ion implantation followed by annealing were studied for the first time. In Fig. Figure 1. shows SEM and RHEED images for the Si/Cu surface before and after implantation of ions with energy E = 1 keV and dose 6×10^{15} sm^{-2} [3]. The surface of non-implanted Si is smooth and has a polycrystalline structure. After implantation of ions, separate cluster phases with a new composition and structure appear on the surface. The surface sizes of cluster phases range from 10 to 20 nm. These phases occupy half of the entire irradiated area.

However, in the electron diffraction pattern, the concentric rings characteristic of polycrystalline films completely disappear, and new, diffuse and wide rings characteristic of

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disordered surfaces are observed. Apparently, it can be assumed that microstresses arising near the cluster phases lead to disorder in non-irradiated areas of the surface. Starting from a dose D ≈ 2 × 10^{16} cm^{-2}, overlapping boundaries of neighboring clusters are observed and, starting from a dose of 10^{17} sm^{-2}, complete doping of the surface layers occurs and an amorphous layer of non-stoichiometric silicon dioxide is formed - in the RHEED picture, instead of concentric rings, one diffuse ring is observed – amorphous halo [4-5].

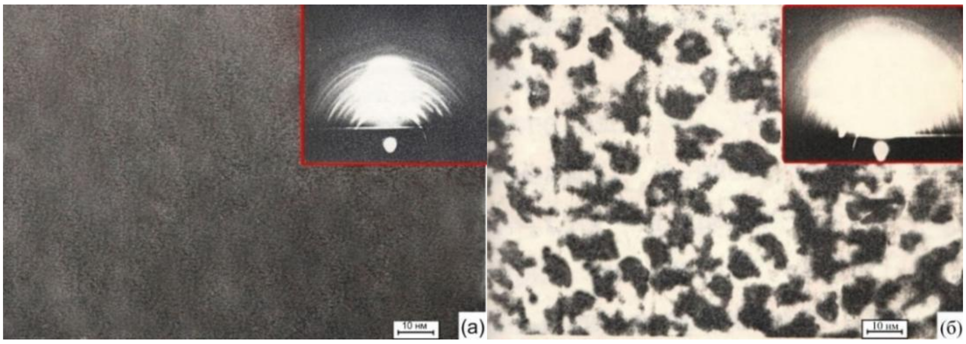


Fig. 1. SEM images and RHEED patterns (insets) for the Si/Cu(100) surface before (a) and after (b) implantation with ions with energy E = 1.0 keV at a dose of 6 × 10^{15} sm^{-2} [3-4].

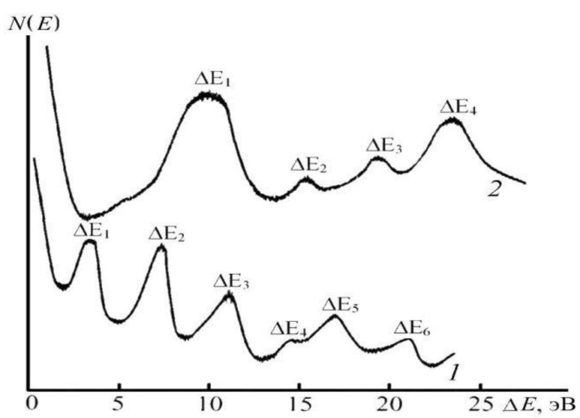
Experimental technique

After heating at a temperature of 750 K, the stoichiometric composition of the SiO_2 film improves significantly (the SiO_2 concentration increases to 85–90 at.%), but the high degree of amorphism remains.

The HPEE spectra of a free-hanging Si/Cu(100) structure before and after the formation of a nano-sized oxide film are shown in Fig. 1. A number of intense peaks are detected in the Si/Cu spectrum. The presence of peaks at energy values ΔE1 = 3.4, ΔE_2 = 6.7 and ΔE_4 = 14 eV can be explained by the occurrence of interband transitions, and other peaks can be explained by the excitation of surface ($\Delta E_3 = \hbar\omega s$ = 10.4, $\Delta E_6 = \hbar\omega s$ = 21 eV) and bulk ($\Delta E_5 = \hbar\omega v$ = 17 eV) plasma oscillations [116; P. 102].

The spectrum of the SiO_2 nanofilm reveals two maxima due to interband transitions ΔE_1 = 9.1, ΔE_3 = 19 eV and two maxima due to plasma oscillations: $\Delta E_2 = \hbar\omega s$ = 15 and ΔE4 = ħωv = 23 eV. Note that the energy of plasma oscillations and interband transitions in a free SiO_2/Si nanofilm differs from the energy in the case of a thick SiO2 film.

Fig. 2. HPEE spectra of the Si/Cu(100) heterostructure before (1) and after (2) the formation of the SiO2 film, Ep = 1000 eV [1-2].



The nature of the shift of the maxima caused by interband electronic transitions is probably associated with the deformation of the functions of electronic states with a decrease in the thickness of the SiO2 film and an increase in the influence of the substrate.

When implanting barium with different doses after annealing, nanophases and layers of barium silicides formed on the Si surface. Nanocluster phases and films (d=20-50 Å) of silicides such as $BaSi_2$ and $CoSi_2$ were obtained.

Thus, after annealing freely hanging Si/Cu films implanted with O_2^+ and Ba^+ ions, three-layer systems SiO_2/Si/Cu and $BaSi_2$/Si/Cu are formed [6-7].

In table Table 1 shows the band energy parameters, maximum values of the secondary electron emission coefficient σm, quantum yield Y of photoelectrons, resistivity ρ of SiO_2 nanofilms and metal silicides. It can be seen that during the formation of metal silicides, the Eg value of silicon decreases by three times, the resistivity by 10^4 times, the values of σm and Y by one and a half to two times, and in the case of the formation of SiO_2, E_g increases by approximately four times, ρ by 300 times, and σm and Y – two to three times [8-9].

Table 1

Zone parameters, σm, Y and resistivity (ρ) of the resulting films

Options	Si, d=400 Å	SiO_2/Si, d=20 Å	$BaSi_2$/Si, d=50-60 Å	$CoSi_2$/Si, d= 50-60 Å
eφ, eV	5.1	3.9	3.1	-
Eg, eV	1.1	4.1	0.3	0.4
ρ, μΩ□cm	$6{\cdot}10^5$	$2{\cdot}10^8$	100-150	80-100
F, eV	5.2	4.9	3.9	4.1
χ	4.1	0.8	3.6	3.7
σm	1.2	2.2	2	1.7
Y	$8{\cdot}10^{-5}$	$6{\cdot}10^{-4}$	$4{\cdot}10^{-4}$	-

Note: eϕ and Φ are thermionic and photoelectronic work functions.

However, these data differ markedly from the data for similar films obtained on the surface of bulk Si films. For example, the Eg value for SiO2 and BaSi2 created on the surface of bulk Si films is 7.9 and 0.7 eV, respectively. These differences are explained by the fact that in films of SiO2 (as well as barium silicides) obtained on the surface of free films, due to the limitation of the annealing temperature, they contain a certain amount of unbound atoms of silicon and oxide of the SiOx type ($1 \leq x < 2$) [7-8].

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