# Subjection of $Si_3N_4$/(111)Si, $Si_3N_4$/(400)GaAs Layers to Synchrotron Radiation

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**Abstract – Modified structure of CVD thin $Si_3N_4$ layers on the (111)Si, (400)GaAs substrates has been studied with use of SR diffraction and electron microscopy techniques. Based on diffraction patterns, existence of $\alpha$-$Si_3N_4$, influence of substrate on the parameters of the layer crystalline lattice, weak bonding between $Si_3N_4$ tetrahedrons as structure fragments of $\alpha$-$Si_3N_4$ were established after subjection to SR dose (200–400 mA min).**

## 1. Introduction

Thin layers of the substances under study ($\alpha$-$Si_3N_4$/(400)GaAs, $\alpha$-$Si_3N_4$/(111)Si) on the different substrates find applications in microelectronics as semiconductors and dielectrics. These materials due to the set of properties such as chemical inertness, mechanical strength, high thermal conductivity and wide energy gap can be used in microelectromechanics. The structural changes in the thin layers are usually investigated with respect to influence of the technological growth parameters (chemical formula of the precursor, partial pressure of its volatile vapors, kind and temperature of substrate and so on) [1–4]. Silicon nitrides microcrystals are synthesized following both traditional routes, by pyrolysis of hexamethyldisilazane HMDS – $Si_2NH(CH_3)_6$, $Me_4SiN_2H_2$ or tetramethylsilazane TMS, and non-traditional rout, in our case as in Ref. [3]. Thin $Si_3N_4$ layer was produced by plasma-chemical reaction of decomposition of HMDS vapors. At low pressure, plasma-activated He* forms various radicals, which promote decomposition of organics. The layers were condensed on single crystal substrates in tunnel-type camera.

The main object of the present work was to study an expected modification of thin silicon nitride layers subjected to diverse doses of white synchrotron radiation (SR) and exposure to various temperatures of thermostatic substrates. For these purposes, phase analysis of thin layers and morphology of their surfaces were studied using a comparison of the experimental and computer-simulated x-ray diffraction patterns, the data of scanning electronic microscopy and electron diffraction before and after SR influence. As a rule, SR was used in lithography to modify the molecular structure of substances with weak chemical bonds and so to change their chemical properties. It is known [6] that exposure of NaCl with strong ionic bond results in evaporation of this substance. In our case, we first carried out the experiment studying possible structure changes in inorganic substances with saturated and directional strong covalent bonds.

## 2. Experimental

Diffraction patterns of silicon nitride layers were obtained with use unique automatic triple-crystal diffractometer (Bragg-Brentano geometry) of high resolution ($2\theta$=0.05°, is half diffraction angle) with monochromatization both of incident and diffracted ($\Delta\lambda/\lambda=4\cdot10^{-4}$) SR beams ($\lambda$=1.5406 A). Surface morphology of the layers was examined with scanning electron microscopy (JSMT-20) and reflection high energy electron diffraction (RHEED) (microscope in regime of electronograph). To visualize surface features such as inclusions specimens are first sprayed with a very layer of gold.

Thin layers on different substrates, (111)Si and (400)GaAs, were synthesized by remote plasma enhanced chemical vapor deposition (RPECVD) of HMDS at various temperatures not exceeding the temperature of layer sublimation. The vapors were transported by helium which in plasma at low pressure formed the radicals capable to store energy and to activate decomposition of HMDS. Diverse SR doses were used to modify the samples under study.

## 3. The structure of $\alpha$-$Si_3N_4$/(400)GaAs

According to RHEED the layers had non-crystalline structure with inclusions of polycrystals. SR diffraction defined the microcrystals structure as polycrystalline $\alpha$-$Si_3N_4$ [1] with the lattice parameters differing from known for polycrystalline state [5].

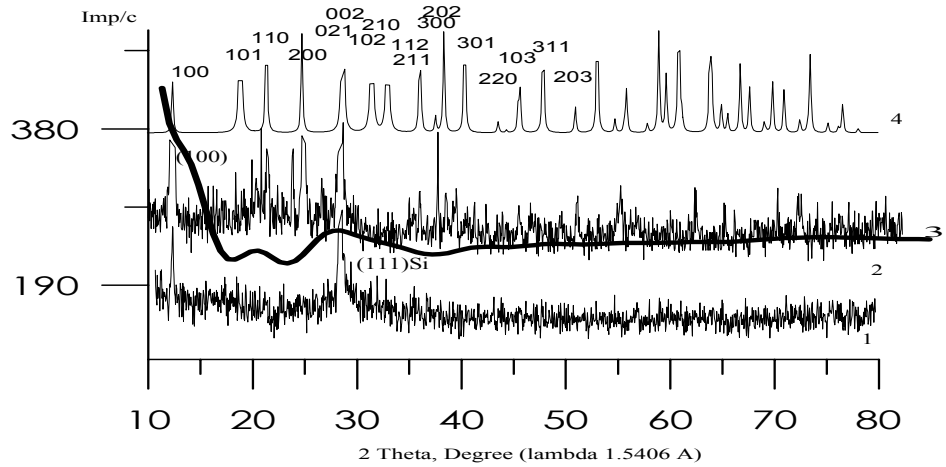


Fig. 1. Diffraction patterns: experimental from $\alpha$-$Si_3N_4$/(400)Si layer before – 1and after SR exposure – 2; 3 – calculated interference part from one $\alpha$-$Si_3N_4$ lattice unit-sized nanocrystals, 4 – diffraction pattern of polycrystalline $\alpha$-$Si_3N_4$ ($a$=8.3, $c$=6.2 A, $\gamma$=120°)

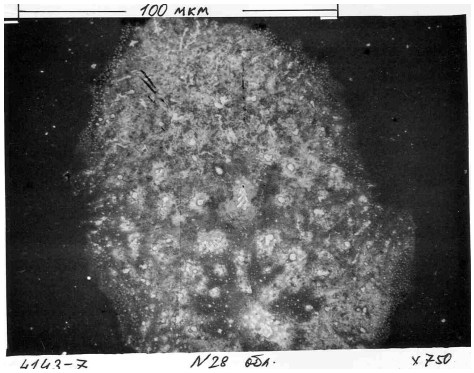


Fig. 2

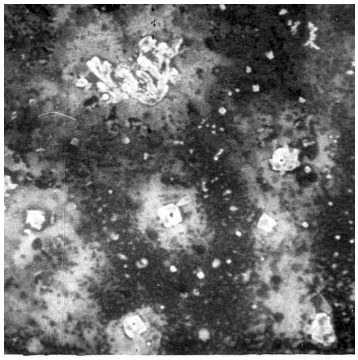

Fig. 3

SEM images of the samples produced at $T$=525 °C in He* atmosphere showed an appearing of uniform amorphous layer, in which irradiation with dose of 417 mA min forms regions (Fig. 2), consisting of microcrystals and dendrites (Fig. 3). The growth of cut microcrystals and dendrites occurs normally to the substrate surface and along the direction of heat abstraction. In the sample obtained at $T$=300 °C these are observable spherical regions formed from the small ring-like yards surrounded by microcrystals along the perimeter (Fig. 4). They were grains of the crystals growing on the substrates. Within yards either microcrystals or dendrites were located. Diffraction patterns showed discrete (100), (200) reflections. After SR exposure (256 mA min) electron microscopy micrographs show the caverns of shape of evaporated (sublimed) microcrystals (Fig. 5). Morphology of inclusions in non-crystalline layer depended on the production conditions of thin layers.

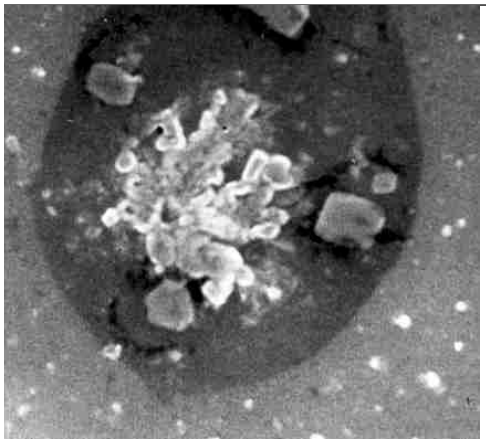

Fig. 4

In addition to RHEED, am-layer was also identified by a shear typical of non-crystalline substances. Reflection positions in experimental XRD patterns of the samples agree with the established parameters of $\alpha$-$Si_3N_4$ structure ($a$=8.3, $c$=6.2 A, $\gamma$=120°). For the sample (Fig. 6, $T$=330 °C, 135 mA min) increasing or reducing of the lattice $\alpha$-$Si_3N_4$ parameters was observed depending on the position shifts to range of large or small diffraction angles. In this sample, it was also found appearing texture, that is, a dependence of (112) reflection intensity on orientation of incident radiation.

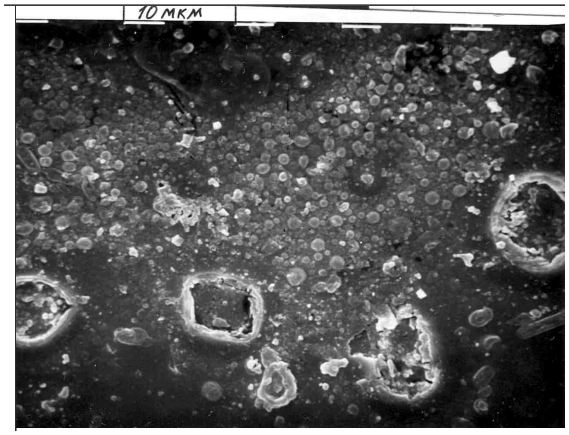


Fig. 5

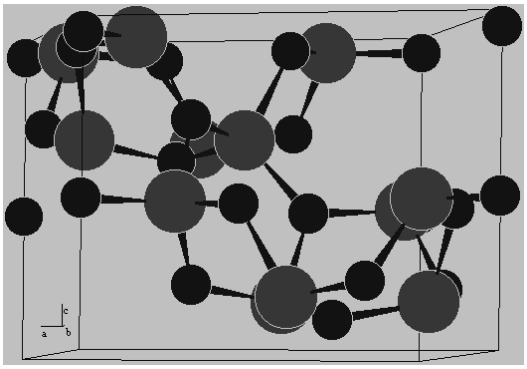

Fig. 6

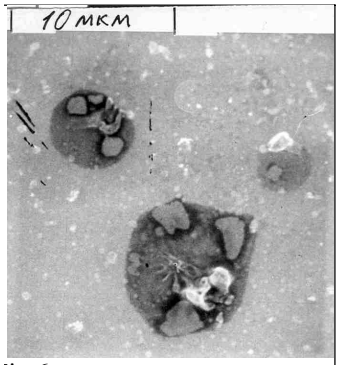


Fig. 7. Lattice unit of $\alpha$-$Si_3N_4$ (space group N159). Size of Si atoms larger than N atoms

Experimental XRD patterns from the layers produced at various substrate temperatures, along with (100), (200) peaks, give different reflections from the proper crystallographic planes of microcrystals of the same $\alpha$-$Si_3N_4$ structure. This indicates the reproducibility of the structure of microcrystals produced by a given synthesis method. We have also observed an influence of the interatomic distances on GaAs surface on the formation of the lattice $\alpha$-$Si_3N_4$ parameters: $a$=8.3 A parameter corresponded to the $r$(Ga-As)=8.3 A substrate distance, i.e. to distances between the atoms on the crystallographic (400) GaAs plane. This suggests that the layer microstructure parameters are dictated by substrate atomic arrangement. The established structure parameters of thin layers differ from the known parameters of polycrystalline state [3]. The samples were produced by decomposition of $Si_2NH(CH_3)_6$.

### 4. The structure of $\alpha$-$Si_3N_4$/(111)Si

As-deposited $Si_3N_4$/(111)Si) (600 °C, 270 °C) layers were seen as uniform surfaces except when separation of polycrystalline $\alpha$-$Si_3N_4$ layer from substrate was observed. The layers have highly ordered (h00) (Fig. 1) $\alpha$-$Si_3N_4$ structure. Irradiated (dose of 120 mA min) $\alpha$-$Si_3N_4$/(111)Si (6000) layer contained two types of $\alpha$-$Si_3N_4$: polycrystalline and nanocrystalline (NC) (NC of one unit lattice ($a$×$a$×$c$)-sized, Fig. 1, curve 5); $\alpha$-$Si_3N_4$/(111)Si (2700) layer (dose of 130 mA min) has the known lattice parameters [2] and diffraction reflections of many times increased intensity that corresponded to heat treatment (SEM showed spherical 2–3 $\mu$m crystals). The samples were obtained by decomposition of $Me_4SiN_2H_2$.

### 5. Conclusion

Observed sublimation of SR irradiated $\alpha$-$Si_3N_4$ microcrystals showed that, at given conditions, SR dose exceeds the energy of chemical bonding of tetrahedral fragments of [$SiN_4$] (Fig. 7). At the same time am-layers were revealed to be valid to SR exposure suggesting existence of silicon carbonitride Si(CN) with strong chemical bond. Microcrystals did not withstand SR dose at normal incident radiation on a (100) $\alpha$-$Si_3N_4$ surface.

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