Properties of planar structures based on Policluster films of diamond and AlN

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Abstract. AlN films doped with zinc were grown on Si substrates by RF magnetron reactive sputtering of a compound target. Policluster films of diamond doped with boron were formed on layered Si/AlN substrates from the gas phase hydrogen and methane, activated arc discharge. By electron microscopy, X-ray diffraction and Raman spectroscopy the composition and structure of synthetic policluster films of diamond and AlN films were studied. Photovoltaic devices based on the AlN/PFD layered structure are presented.

1. Introduction
A layered structure on the basis Policluster films of diamond (PFD) and aluminum nitride (AlN) are promising for their use in devices of the microwave acoustoelectronics, in photodetectors of ultraviolet range and other devices of electronic equipment [1]. The layered structure of the PFD/AlN, doping metal impurities and nitrogen ions may alter the structural properties of the PFD to give them the inherent properties of semiconductors with high mobility of charge carriers [2, 3]. Such materials are needed to create functional radiation-resistant semiconductor devices. In such structures the AlN layer serves as a layer with n-type conductivity [4]. Diamond-like film coating formed in vacuum by sputtering of carbon target in high frequency (HF) magnetron and arc discharges [5, 6]. In [5] it is shown that during ion doping of carbon coatings is the formation of CNx compounds with a prevailing content of sp²-phase with reduction of the cluster size. By doping with metal atoms and nitrogen it is possible to modify the structural and mechanical properties of diamond-like films. Technological impact of the components of the plasma treatment of the films leads to creation of additional defects and amorphization of the structure [7, 8].

The influence of fabrication regimes on the structure and composition Policluster films of diamond and AlN films that determine the performance characteristics of the photodetectors based on the structure of the PFD/AlN was studied.

2. Samples and research methodology
Samples in the form of a planar layered structure of Si/AlN/PFD on a substrate of single crystal silicon was formed by consistent growth of AlN films and the PFD on the substrate of Si{111}. First an AlN layer was formed by HF magnetron reactive sputtering of aluminum Al in the environment, gas composition of Ar+ (40...60) % vol. N₂ at a pressure of ~ 0,6...0,9 Pa. Power radio-frequency
discharge at a frequency of high-frequency discharge of 13.56 MHz at a voltage of 200...350 V was ~ 1.5 to 3 kW. The magnitude of the electric displacement on the substrate when distance target–substrate of 60 mm was 30 V. The growth rate of the AlN film at substrate temperature 450...570 K was ~ 3 µm/h. In the growth process, the AlN film was doping by zinc (the structure Si/AlN:Zn) to give it semiconductor properties. A composite target of Al and Zn plates were an area of 0.1...0.3 % of the area of the sputtering target.

On substrates of Si/AlN:Zn grown Policluster films of diamond from the gas phase H₂ and CH₄ in the activated arc discharge in the gas medium composition (1.5 to 4) % CH₄+H₂ at a pressure of > 10⁴ Pa, the discharge power of 1200...1500 W. The growth rate Policluster films of diamond substrate at a temperature of 1100 to 1470 K was ~ 20 µm/h. The Layer of PFD in the process of growth was doping by evaporation of the bromine from the graphite container at a temperature of ~ 850 K.

On the surface structure of the AlN/PFD magnetron sputtering of Ti in Ar applied a translucent film of Ti with a thickness of ~ 40 nm at a pressure of 9.3 Pa. The substrate is pre-annealed luminous flux by the method of [9].

3. The structure of the films

The structure of the obtained films was investigated a method of raster microscopy using electron microscope (REM) Carl Zeiss Supra 40-30-87 and X-ray diffractometer Rigaku D/MAX-2500/PC (Сквα-радиация). Raman spectra films of AlN/PFD using a spectrophotometer type LabRAM HR 800 He-Ne laser emitting 632.8 nm were studied. The concentration of dopants in the AlN films and the PFD controlled on the device CAMEBAX electron microprobe spectral analysis. The concentration of impurities in the AlN films was controlled separately as in X-ray amorphous and crystalline phases by Stripping voltammetry method and methods of selective dissolution of the phases of the film layer.

4. Results and their discussion

In Figure 1 shows X-ray diffraction pattern of the layered structure of Si/AlN/PFD when the thickness of the films: PFD – 12 µm; AlN – 3,6 µm.

The structure of the planar film of nanostructures Si/AlN/PFD are a mixture of amorphous and crystalline phases.

![Figure 1](image)

**Figure 1.** X-ray diffraction pattern from a layered structure of Si/AlN/PFD. The intensity peak of the scattered radiation corresponds to: 1 – 111 Si; 2 – 0002 AlN; 3 – 111 Diamond; 4 – 0004 AlN; 5 – 220 Diamond; 6 – 311 Diamond.

X-ray diffraction pattern obtained from structures with Si/AlN/PFD (Figure 1) showed the presence of crystalline phases of AlN spatial P63mc group and diamond group Fd3m. The crystallinity of the AlN films depends on technological modes of their formation and was 0...90 % vol. in the layer, and Policluster films of diamond were > 99 % vol.

During forming films of AlN layer is formed of polycrystalline phase fibrous (columnar) structure with orientation of the fibers in the direction of the texture axis <0001>. Axial columnar texture is formed depending on the sequence of the subsequent growth stages: emergence, coalescence of nuclei, geometric selection and reduction orientation between crystallites. Formation of AlN films in
the direction of <0001> is determined by the atomic roughness of the growth surface. The growth layer of the AlN film proceeds in the direction <0001>, which coincides with the direction of the screw axis of the symmetry 6\_3. This structure represents the composite reinforced thin needle-like fibers with strongly roughened side surface, the spaces between them completely filled with them coherent X-ray amorphous phase. According to REM needle fiber diameter is ~ 0.2 \(\mu\)m. Axis orientation <0001> texture relative to the surface of the substrate is determined by the flow direction of particles deposited particles in the layer. The fibers in the film consist of a group of coherent fibers. In terms of the broadening of diffraction peaks and calculated the crystallite size of crystalline phase of doped AlN films is 15...50 nm, and the undoped – is 35...65 nm when the axial orientation of textured crystallites with respect to the axis texture < 3°.

Studies of PFD films by REM showed that they consist of grains elongated in the growth direction with a transverse size of 2 to 8 \(\mu\)m on the surface of the layer. Film PFD possess two conical texture: <111> (with angle polarstar cone ~ equal to 8°) and <110> (~ 17.5°) with lamellar structure of the grains. The size of crystallites in doped and undoped boron films PFD depends on the temperature of their synthesis. So when the film thickness of 20 to 200 nm grains formed corresponding to the thickness of the layer.

In Figure 2 shows Raman spectra Policluster films of diamond (a) of thickness \(h = 12 \mu\)m AlN films (b) with a thickness of \(h = 3.2 \mu\)m. The prepared films were legionares Zn (curves 1 and 2). 1 Film contain additional phase Zn and ZnN\(_x\) (curves 1) with crystallinity \(J < 10 \% \text{vol.}\) and in the absence of additional phases (2) when \(J \approx 40 \% \text{vol.}\) and undoped AlN film (3) has a crystallinity \(J \approx 80 \% \text{vol.}\).

![Figure 2. Raman spectra Policluster films of diamond (a) and AlN films (b).](image)

In the Raman spectra (Figure 2a) doped films, the PFD has an intense diamond band at the KR \(\Delta\nu\) is equal to 1333 cm\(^{-1}\) with strip half-width \(\Delta\nu_{1/2} = 3.4...4.5\) cm\(^{-1}\). The intensity of the band diamond phase is much more intensity blurred bands of diamond-like carbon (~ 1550 cm\(^{-1}\)). View the Raman spectra of the AlN films depends on the structure of the structure (Figure 2b). Form, intensity and location of bands in the Raman spectra for AlN films obtained are substantially different under various technological regimes. The observed broadening of the bands (\(\Delta\nu_{1/2} > 100\) cm\(^{-1}\)), characteristic for the crystal structure and the appearance of additional bands speaks about x-ray amorphous structure of the films. The periods of the lattice of undoped AlN films on 0.06...0.86 % higher than the theoretical value. In the adsorption layer of the formed film is observed in the interaction of ions N, Al and Zn, formed in the high-frequency discharge plasma. The increase in the concentration of dopant in the films of AlN decreases the degree of crystallinity and at a concentration of ~ 2 at. % does not exceed ~ 15 % vol. Alloying impurity in the AlN film is in the form of individual atoms in crystalline and in amorphous phases. The X-ray amorphous inclusion Zn and Zn\(_3\)N\(_2\) are located along.
the boundaries of fibers. The concentration of Zn in the AlN films depends on the ratio of the area of spray target areas of the plate Al and the impurity source of Zn, and the coefficients of their spraying. By electron-beam probe spectral analysis to determine the content of Zn in the doped AlN films, which is > 3 wt %. According to the analysis of X-ray amorphous phase of AlN, the content of Zn is 0.72 wt %. The main share falls on the impurity amorphous Zn and ZnN. The periods of the lattice of the crystalline phase of AlN films: Zn in the degree of crystallinity of ~ 12 % vol. and concentration of Zn to ~ 2 wt %. less than the theoretical. Clearly defining the conductivity type are point defects interstitial impurity Zn. in the crystalline phase AlN.

The resulting films of PFD had p-type conductivity with the maximum concentration of boron atoms (up to ~ 4 \cdot 10^{19} \text{ cm}^{-3}) with the activation energy of electrical conductivity of ~ 0.1 eV.

5. Film photodetector

In Figure 3 shows graphs of the voltage on the pads of layered nanostructures AlN:Zn/PFD:B upon irradiation with light in the UV range. Policluster films of diamond is obtained at temperatures: 1 – 1250 K; 2 – 1400 K.

![Figure 3. The voltage appearing on the pads the layered structure AlN:Zn/PFD:B during UV-irradiation.](image)

During exposed to UV irradiation on the pads (layer semitransparent Ti) layered structure AlN:Zn/PFD:B, giving the voltage to 1.2 V (Figure 3). In the studied heterostructures, the AlN layer contained the total Zn concentration of ~ 0.16 at. % (the ratio of concentration of Zn in the amorphous and crystalline phase in the AlN film was of ~ 2.5 when the degree of crystallinity of about 40 % vol.). The concentration of boron in the PFD was estimated to be ~ 1019 cm\(^{-3}\). AlN nanostructures:Zn/PFD:B in which the formation of the PFD layer was carried out at temperatures > 1300 K have a lower sensitivity when exposed to UV radiation.

6. Conclusions

The obtained layered planar structures Si/AlN/PFD on silicon substrates by sequential deposition in vacuum of layers of films of AlN and PFD by methods of HF-magnetron reactive sputtering and arc discharge. During the deposition of AlN films and the PFD have been alloying zinc and boron, respectively. Film structure is AlN/PFD during irradiating with light of the UV range generates an electrical signal of amplitude 1.2 V. The combination of Policluster films of diamond with films of other wide bandgap semiconductor materials in planar layered structures allows you to create new passive and active nanostructures for solid-state microelectronics.

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