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Diamond films obtained on silicone substrates by the CVD method and properties of structures based on them

A.S. Saidov, A. Kutlimratov, Sh.N. Usmonov and U.Kh. Rakhmonov*

Physical-Technical Institute of Academy of Sciences of Uzbekistan, Tashkent, Uzbekistan
*e-mail: fti_uz.@mail.ru

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At present, the technology of obtaining diamond films on silicon and other substrates is well studied. However, in all published works to date, there has been no report of a layer of silicon carbide formed between the diamond film and the silicon substrate. The presence of a layer $(15R\text{-}SiC)_{1-x}(C_{diamond})_x$ in the structure was revealed in the studies of structures with a diamond film obtained by us on silicon substrates by chemical vapor deposition. Diamond films were obtained on single-crystal silicon substrates with (111) orientation and n-type conductivity by the well-known CVD technology in a hydrogen-methanol (CH_3OH) mixture with the addition of a certain amount (know-how) of ammonia (NH_3). The diamond films consisted of small single crystals 3–5 μm in size, closely interlocked and constituting a continuous film. When studying the current-voltage characteristics of structures created on the basis of the obtained diamond films, a blue-white glow with a blue-violet tint was observed, which is explained by the mixing of blue-violet photons with photons re-emitted in the diamond film.

Key words: CVD technology, diamond film, silicon substrate, silicon carbide layer, current-voltage characteristic, electroluminescence.
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1 Introduction

It is known that diamond has such unique properties as the highest hardness and thermal conductivity, chemical resistance, high light refractive index, and others among all known crystalline materials [1–3]. Most importantly, diamond is a semiconductor with a band gap of ~5.5 eV [3, 4], due to which it is transparent in almost the entire range of the solar radiation spectrum, which makes it in demand for use in most micro- and optoelectronic devices, including photovoltaics. In the creation of electronic devices, its epitaxial films are mainly used, grown on different substrates using various methods. Because, despite the small thickness (several micrometers), diamond films exhibit all the properties and advantages inherent in its bulk crystal. Epitaxial diamond films are used to create transistors operating in the microwave range [5], solid-state detectors [6], high-voltage and high-temperature diodes [7], and others.

All epitaxial diamond films are p-type semiconductors with an impurity activation energy of 0.35–0.38 eV [4, 8]. The diamond band gap for indirect transitions is 5.5 eV, and for direct transitions – is 7.4 eV [7, 9]. If we add to this that the bright and very diverse luminescence of diamonds has been known for a long time [10], then one could think about creating light-emitting diodes and lasers based on it. However, to date, mass production of none of the semiconductor devices has been established, neither on the basis of its bulk crystals nor on the basis of its epitaxial films.

There is an assumption that it is possible to use diamond films in silicon solar cells both as a transparent conductive «window» and as an active working layer. For example, the authors of [11] state that impact ionization processes and radiative transitions in the conduction band of diamond are possible due to the excess energy of electrons generated by short-wavelength photons and the formation of additional eh pairs. In addition, the diamond layer, absorbing short-wavelength photons, can re-emit their energies in the form of long-wavelength photons, which can be absorbed in silicon layers [11].

In connection with the above, in this work we tried to show the production of diamond films by the simplest and most accessible CVD method and the possibility of using them in the structures of semi-

conductor devices, including solar cells. In this work, we studied the properties of diamond films obtained on n-type silicon substrates with (111) crystal orientation.

To date, there is a large amount of experimental data in the literature on the production of diamond films by the CVD method [12–15], however, they are often quite general in nature, and many details of the processes of formation of diamond crystallites that make up films remain not fully understood. For example, in the literature, we did not find data on the silicon carbide (SiC) transition buffer layer formed in the region between the diamond film and the silicon substrate.

2 Materials and methods

There are various methods for producing diamond films. For example, in [16-20], diamond films were obtained by the gas-phase method using a microwave discharge. A group of researchers from the Research Institute of Inorganic Materials (Japan) [16] created a setup that makes it possible to grow diamond films even on non-diamond substrates in a continuous flow of a gas mixture excited by a microwave discharge near the substrate front, which made it possible to increase the growth rate. The authors used silicon (semiconductor), molybdenum (metal), and quartz glass (insulator) plates as substrates [17].

In the experiments carried out within the framework of this article, diamond films were obtained by chemical vapor deposition (CVD) using the technology described in [18, 19]. Silicon wafers with dimensions of 10 ´ 10 ´ 0.3 mm, cut in the (111) direction from n-type single-crystal silicon with a specific resistance of ~10 Ω cm, were used as substrates. The technological modes of the epitaxy process were chosen from the results of our previous experiments on growing diamond films by the CVD method on silicon substrates [20, 21].

It is known that the quality of pre-treatment of the substrate surface significantly affects the structural perfection, physical and optical properties of the epitaxial layers obtained on them. One of the many ways to treat the silicon surface before epitaxy is hydrogen etching [22]. Therefore, we also applied this method to clean the surface of silicon substrates immediately before the epitaxy process.

Hydrogen etching of the surface of the silicon substrate was carried out at a temperature of tungsten filaments – 1800°C for 3 min. In this case, the hydrogen flow was 1000 cm3/min, and the linear hydrogen flow rate was 30 cm/min, with a reactor diameter of 60 mm. This method made it possible to optimally clean the surfaces of silicon substrates. The process of cleaning the surface of the silicon substrate from SiO_2 will occur according to the following reaction. Since atomic hydrogen (H), being active, quickly reacts with oxygen of silicon dioxide (SiO_2) and, at the same time, water vapor (H_2O) is formed according to the reaction: $SiO_2 + 4H$ ® $Si + 2H_2O$. Water vapor is carried away from the surface of the substrate by the gas flow. As a result of the purification process, dangling silicon atoms appear on the surface of the silicon substrate, which, during the deposition of diamond layers, capture carbon atoms and form silicon carbide (SiC) molecules. In turn, the latter form continuous thin layers of SiC over the silicon substrate, which is confirmed by the Raman scattering spectrum (this will be discussed below).

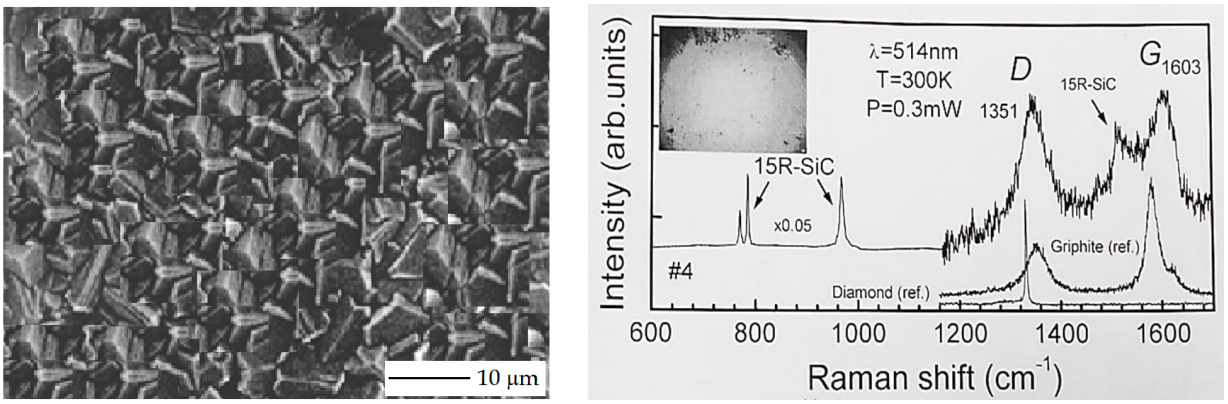
During the deposition of diamond films, the following CVD technological regimes were observed: the temperature of the tungsten filaments was maintained within 2100–2150°C, and the substrate temperature was within 850–900°C, the total flow of the gas mixture ($CH_3OH + H_2 + NH_3$) was 50–60 cm^3/min and its pressure was maintained within the range of 50–60 Torr, the temperature of methanol in the bubbler was maintained within the range of 33–35°C, and the hydrogen/methanol ratio in the total gas flow in the reactor was 0.5–1.0%.

In the process of growth, nucleation will initially occur before the formation of a continuous film begins and, in this case, growth will occur on different faces of the nucleus at different rates. In addition, as a result of the gradual reaction of the hot filaments or due to any other changes in the reaction conditions, the growth rate may change. In experiments, the average growth rate was 0.2–0.3 μm/h. At the same time, there was no significant difference in the deposition rate between doped and undoped diamond films.

The existence of a diamond film was established by measuring the microhardness, studying the structural perfection of the diamond film on a Jeol JSM-5910LV scanning electron microscope with a JED-2200 Jeol X-ray analysis system (Japan) and the Raman scattering spectrum in the energy range corresponding to diamond peaks. Recording conditions: accelerating voltage 20 kV, probe current 1 nA, and also by the Hall method. The grown diamond films were polycrystalline, which consisted of crystallites with a grain size of 2–3 μm, which were individual single crystals (Fig. 1*a*).

To determine the crystal structure of the grown diamond film, Raman spectra of Raman scattering

(Raman) were taken at room temperature (300 K) when the samples were irradiated with a laser beam with a wavelength of 514 nm. The Raman analysis showed that the peak of the 15R-SiC silicon carbide polytype is observed in the spectrum (Fig. 1*b*). We assume that this peak belongs to the 15R-SiC silicon carbide polytype, which is formed at the beginning of the diamond film growth process, that is, at the beginning of the diamond film growth, C atoms are deposited on the Si substrate and bond with Si atoms with dangling bonds located on the surface of the Si-substrate and thus form 15R-SiC molecules. We do not yet know the formation mechanisms of exactly the 15R-SiC polytype, however, according to the literature data, it can be assumed that 15R-SiC is formed precisely between carbon- and silicon-containing layers (in our case, between silicon and diamond). As the layer thickness increases, the number of 15R-SiC molecules gradually decreases, since the formed 15R-SiC layer prevents the passage of carbon atoms to silicon. However, in the reactor in the gaseous medium there are silicon atoms isolated from the quartz of the reactor, which, getting into the growing layer, participate in the further formation of the $p(15R\text{-}SiC)_{1-x}(C_{diamond})_x$ solid solution, that is, the layer where the number of molecules is 15R -SiC gradually decreases, and the amount of carbon increases. Thus, the heterostructure $nSi - p(15R\text{-}SiC)_{1-x}(C_{diamond})_x$ is formed. This is evidenced by a broad peak at 1351 cm^{-1} (Fig. 1*b*), which corresponds to the polycrystalline structure of the diamond film. Fig. 1*b* also shows that the spectrum contains a broad 15R-SiC peak, which also indicates the polycrystalline structure of the structure, indicating the formation of a $(15R\text{-}SiC)_{1-x}(C_{diamond})_x$ solid solution. As can be seen from fig. 1a, the film was obtained with clearly faceted crystals, uniformly covering the entire surface of the substrate and having a fine-grained polycrystalline appearance.



а) б)

Figure 1 – Surface (*a*) and Raman spectrum (*b*) of a diamond film grown on a silicon substrate with (111) crystal orientation

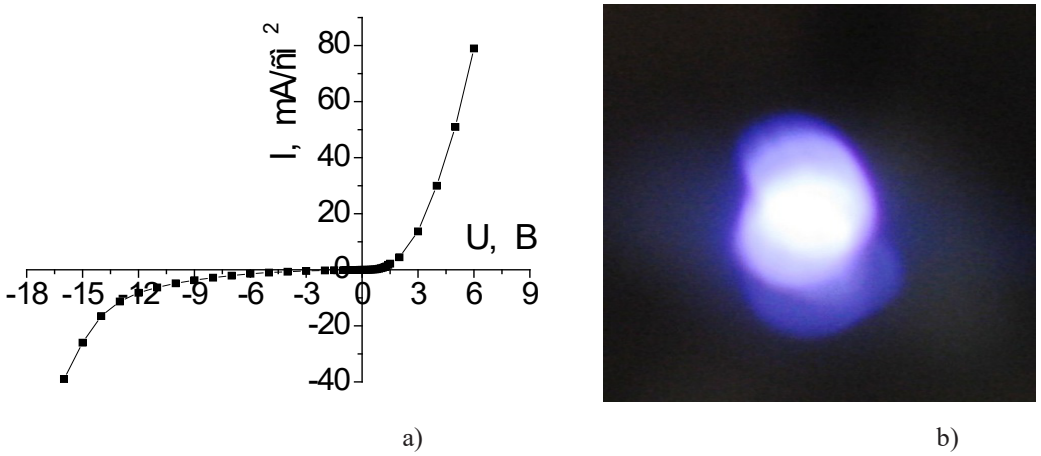
The results of Hall measurements showed that the grown films, despite the fact that ammonia was introduced into the gas mixture, that is, the film was doped with nitrogen, still they have p-type conductivity with a charge carrier concentration of $(2\text{-}4)\cdot10^{17}$ cm^{-3} and electron mobility within 950–1010 $cm^2/(V\cdot s)$, which is noticeably higher than in our previous works [20, 21]. Here, the decision to introduce nitrogen impurities was made with the consideration that at present a large number of scientific studies are aimed at creating computers based on quantum informatics, the unit (qubit) of which is a small-sized system. One of the most actively studied contenders for this role is the negatively charged nitrogen-vacancy defects NV– in diamond [23]. In addition, as described in [24], NV centers are highly efficient photon emission centers, which allows them to be used to create efficient LEDs and lasers, to obtain information about the state of the spin and optically control its state, as well as to detect the spin state. other materials [25]. In this case, it is necessary that the dimensions of the atoms introduced into the diamond crystal lattice correspond to the dimensions of the carbon atom. From this point of view, nitrogen (N) atoms are suitable

candidates for this role. Nitrogen creates fairly deep donor energy levels in the band structure of diamond (1.7 eV from the bottom of the conduction band), but, nevertheless, it is often used to dope diamond due to the fact that nitrogen is widely available and non-toxic [23]. The introduction of nitrogen atoms into diamond is not the only purpose of obtaining electronic conductivity.

3 Results and discussion

The dark current-voltage characteristics of the nSi – $p(15R\text{-}SiC)_{1-x}(C_{diamond})_x$-heterojunction were measured, the results of which are shown in Fig. 2. It can be seen from Fig. 2*a* that the breakdown of the p-n-junction with reverse bias occurs at voltage of ~14-15 V. breakdown of the reverse current-voltage characteristics (Fig. 2*a*).

The glow (Fig. 2*b*) observed under conditions of breakdown of the nSi – $p(15R\text{-}SiC)_{1-x}(C_{diamond})_x$ heterojunction is explained as follows. Apparently, during the breakdown of the n – p-junction, electroluminescence of blue-violet photons occurs, which is noticeable in the blue-violet contour of the glow. These photons, in the course of propagation in the $p(15R\text{-}SiC)_{1-x}(C_{diamond})_x$ layers, are absorbed both in the $p(15R\text{-}SiC)_{1-x}(C_{diamond})_x$ layer and in absorption centers formed due to crystal defects $p(15R\text{-}SiC)_{1-x}(C_{diamond})_x$ solid solution lattices and generate excitons. In turn, these excitons recombine with the emission of long-wavelength photons, as shown in [26, 27]. As a result of mixing these photons with blue-violet photons, whitish-blue light is produced, shown in Fig. 2*b*. These photons can penetrate inside the structure and be absorbed in the silicon layer and generate electron-hole pairs, which, being separated at the nSi – $p(15R\text{-}SiC)_{1-x}(C_{diamond})_x$ heterojunction, can participate in the generation of photocurrent. Such a process can also occur when the nSi – $p(15R\text{-}SiC)_{1-x}(C_{diamond})_x$-heterostructure is illuminated by sunlight. If we take into account the fact that the $p(15R\text{-}SiC)_{1-x}(C_{diamond})_x$ layer has sufficient conductivity (since the concentration of charge carriers is $(2\text{-}4)\cdot10^{17}$ cm^{-3}, and the electron mobility is 950-1010 $cm^2/(B\cdot sec)$, then it can be used as a conductive transparent "window" and active layer, as well as a protective coating for silicon solar cells used in space conditions, where high-energy photons prevail.



a) b)

Figure 2 – Current-voltage characteristic (*a*) and photography of the white glow (*b*) of the nSi – $p(15R\text{-}SiC)_{1-x}(C_{diamond})_x$ heterostructure. The photography was taken with a Coolpix E3200 electronic digital camera from Nikon (Japan)

As is known, diamond belongs to indirect-gap semiconductors, in which the probability of interband transitions occurring with conservation of momentum is very low. Consequently, radiative recombination in them proceeds in accordance with fig. 3, that is, through impurity centers [28]. Therefore, according to the theory of absorption, short-wavelength photons with energies less than the band gap of the solid solution $(15R\text{-}SiC)_{1-x}(C_{diamond})_x$ (> 3.013 eV, 15R-SiC polytype), but greater than the ionization energy of absorption centers (fig. 3) (formed due to defects in the diamond crystal lattice) pass without being absorbed through the diamond film and are partially absorbed by the 15R-SiC layer, and create excitons in the heterostructure nSi – $p(15R\text{-}SiC)_{1-x}(C_{diamond})_x$. These excitons recombine after

some time by emitting photons that can be absorbed in silicon. In a word, in the $(15R\text{-}SiC)_{1-x}(C_{diamond})_x$ solid solution layer, the effect of "re-emission" of short-wavelength photons into long-wavelength photons absorbed by silicon occurs. In addition, short-wavelength photons with an energy greater than the ionization energy of diamond absorption centers can also be absorbed in these centers and also form excitons, which can also recombine after a while by emitting long-wavelength photons absorbed in silicon. Thus, short-wave photons are converted into long-wave ones, which is important for solar cells for space purposes. Such structures can be successfully used to convert solar energy in space conditions, since diamond has good photosensitivity in the wavelength range of 0.2–1.2 μm [26]. In addition, the diamond film itself can absorb high-energy photons and generate minor charge carriers, and can contribute to the efficiency of a solar cell. In addition, due to the resistance of diamond to cosmic radiation, solar cells coated with a diamond film can work longer in harsh space conditions.

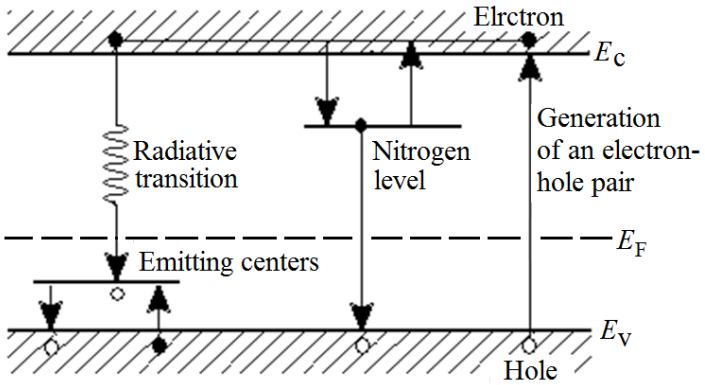


Figure 3 – Processes of radiative and nonradiative recombination [28]

4 Conclusions

Films of $p(15R\text{-}SiC)_{1-x}(C_{diamond})_x$ diamond solid solution are grown on silicon substrates by the CVD method. It is shown that, in this case, a $p(15R\text{-}SiC)_{1-x}(C_{diamond})_x$ transition buffer layer is first formed on the silicon substrate due to the chattering bonds of silicon atoms formed during the cleaning of the silicon substrate surface by hydrogen etching. We have not yet been able to determine the thickness of the transition buffer layer.

A whitish-blue glow noticeable to the naked eye in the region of breakdown of the inverse current-voltage characteristic was found, which is explained by the electroluminescence of blue-violet photons during the breakdown of the nSi – $p(15R\text{-}SiC)_{1-x}(Cdiamond)_x$ heterojunction. These photons, propagating in the $p(15R\text{-}SiC)_{1-x}(Cdiamond)_x$ layer, are absorbed in absorption centers formed due to crystal lattice defects and generate excitons. Excitons recombine and emit relatively long-wavelength photons, which, when mixed with blue-violet photons, produce whitish-blue light, as shown above. Photons can penetrate inside the structure and be absorbed in the silicon layer and generate electron-hole pairs. Such structures can be successfully used in the manufacture of solar cells operating in space conditions. Since the composition of the spectrum of solar radiation incident on the surface layers of the atmosphere is dominated by higher-energy photons, which, being absorbed in the layers of the $p(15R\text{-}SiC)_{1-x}(Cdiamond)_x$ solid solution, convert them into long-wavelength photons absorbed in silicon and, thus can contribute to efficiency.

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