

## CONDUCTIVITY OF POLYCRYSTALLINE DIAMOND FILMS

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In recent years much progress has been made in the synthesis of diamond<sup>1-4,6,7)</sup> and diamond-like carbon films.<sup>5)</sup> Works have been published on the study of conductivity of diamond films grown from thermally and electrically activated gaseous phase on diamond and nondiamond substrates.

The electrical resistivity of nondoped epitaxial films grown from the thermally activated gaseous phase is  $10^{12}$ – $10^{13}$   $\Omega\cdot\text{cm}$ .<sup>3)</sup> The minimum resistivities of semiconductive epitaxial diamond films doped with boron (p-type) and phosphorus (n-type conduction) at 300 K are  $10^{-3}$  and  $10^1$   $\Omega\cdot\text{cm}$ , respectively.<sup>6)</sup>

The transverse resistance of polycrystalline diamond layers grown on the molybdenum substrates from a hydrocarbon–hydrogen mixture activated by HF-induction discharge was measured at room temperature by Matsumoto.<sup>7)</sup> The resistivities of films grown at the crystallization temperatures  $T_c=800$  and  $940^\circ\text{C}$  are equal to  $10^{10}$  and  $10^8$   $\Omega\cdot\text{cm}$ , respectively.

In the present work the method of chemical crystallization from electrically activated gaseous phase<sup>8)</sup> has been used for the synthesis of polycrystalline diamond films. Crystallization has been performed in a flow reactor under a pressure of 75 Torr; the initial mixture consisted of  $\text{CH}_4$  (3 vol.%) and  $\text{H}_2$ . 11–17  $\mu\text{m}$  thick films have been grown on polycrystalline tungsten substrates of the size  $6\times 8$   $\text{mm}^2$ . Over the whole crystallization temperature range  $T_c=800$ – $1200^\circ\text{C}$  faceted growth forms of crystallites have appeared, which constitute the diamond layer. The maximum size of crystallites observed on the growth surface has been nearly proportional to the thickness of the films, equal to 10–20  $\mu\text{m}$ .

The temperature dependence of the transverse electrical conductivity of diamond films  $\sigma(T)$ , has been studied. The measurements of  $\sigma(T)$  have

been taken at a constant voltage in the two-electrode circuit. The tungsten substrate represented one contacts, while the other was made by evaporating silver or depositing a suspension of colloidal graphite-aquadag. The measurements were made in vacuum  $10^{-4}$  Torr. Over the studied temperature range  $300\leq T\leq 1000$  K, no irreversible change of conductivity was observed, which is indicative of a considerable difference of polycrystalline diamond layers from the films of diamond-like carbon, whose electrical properties change irreversibly, usually upon heating up to  $300^\circ\text{C}$ . The breakdown voltage of high ohmic ( $10^{12}$ – $10^{13}$   $\Omega\cdot\text{cm}$ ) diamond films exceeds  $10^6$  V/cm.

The current-voltage characteristic of one of the samples under study, presented in Fig. 1, has the shape typical of the currents limited by the space charge. The linear part of the current-voltage characteristic, where  $I\sim U$ , is followed by the region  $I\sim U^n$  ( $1.5<n<3$ ). The  $\sigma(T)$  dependence was obtained at low electric field intensity in the ohmic region of the  $I$ – $U$  characteristics.

The crystallization temperature  $T_c$  is the parameter of the family of the dependences  $\log\sigma(1/T)$  presented in Fig. 2. As is seen in Fig. 2, the conductivity of the diamond polycrystalline layer is of activation character. For all the temperatures of crystallization up to  $1100^\circ\text{C}$ , the conductivity was determined by two activation energy values  $E_L$  and  $E_H$ , which correspond to the low and high temperature regions of the measurements. For the films grown at  $T_c=(800$ – $900)^\circ\text{C}$  the activation energy of conductivity  $E_L=0.5\pm 0.05$  eV over the

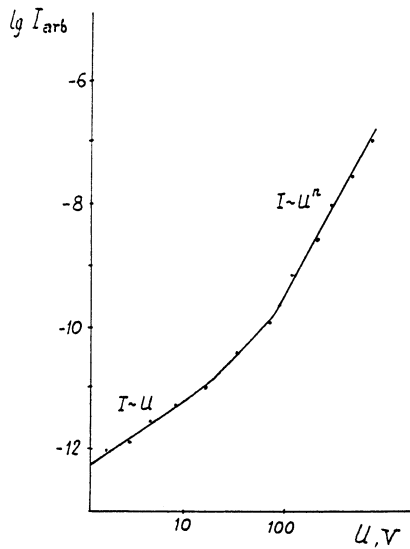


Fig. 1. Current-voltage characteristics of diamond film at room temperature.

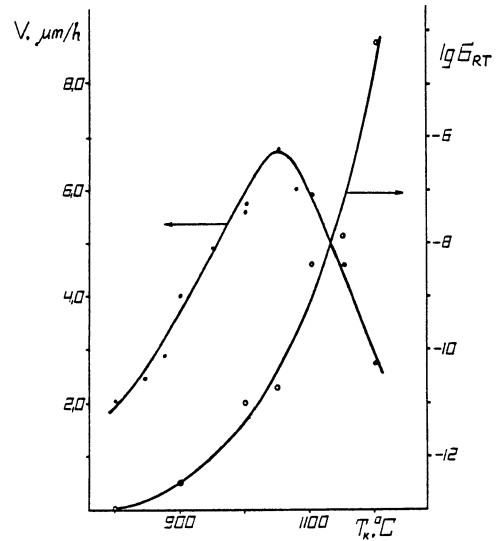


Fig. 3. The room temperature conductivity and the growth rate of diamond films as functions of  $T_c$ .

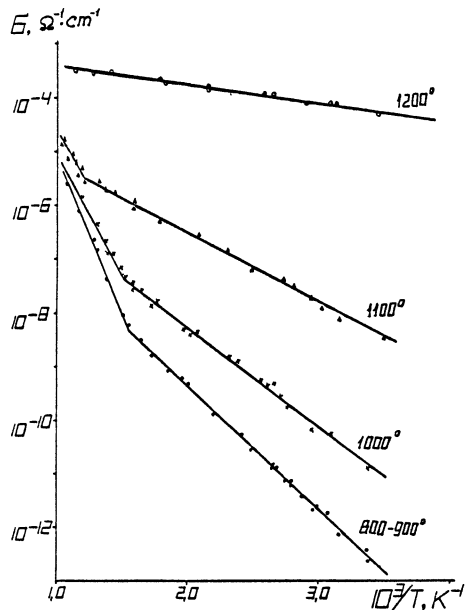


Fig. 2. The temperature dependences of the transverse conductivity of the diamond films grown at different temperatures of crystallization.

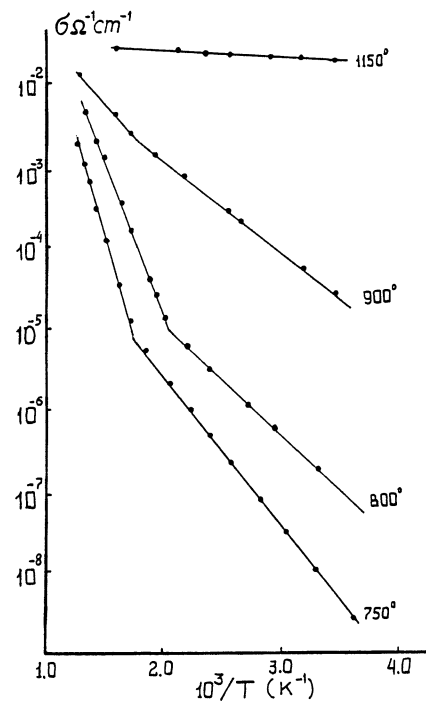


Fig. 4. The temperature dependence of the longitudinal conductivity of diamond films grown at different  $T_c$  (on dielectric substrates).

range  $300 \leq T \leq 600$  K and  $E_H = 1.15$  eV over the range  $600 \leq T \leq 1000$  K.

At  $T_c \geq 900^\circ\text{C}$  the character of the  $\log \sigma(1/T)$  changes: the conductivity increases and the  $E_L$  and  $E_H$  values decrease. For the films synthesized at

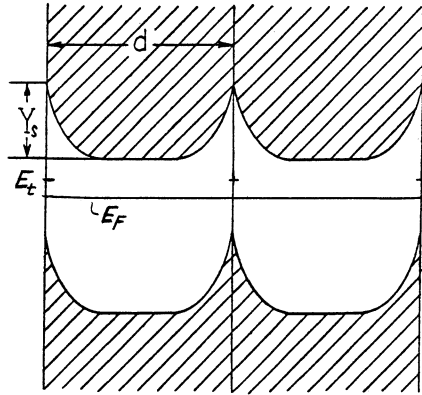


Fig. 5. The band diagram of polycrystalline diamond film.  $d$ , crystallite dimension;  $E_F$ , Fermi level;  $E_t$ , trapping states.

$T_c = 1200^\circ\text{C}$ , the conductivity is still of activation character:  $E \cong 0.1$  eV over the whole range  $300 < T < 1000$  K. The  $T_c$  effect on the room temperature electrical conductivity of films, and growth rate of diamond films (V) are shown in Fig. 3.

The effect of the crystallization temperature on conductivity is, obviously, due to the change of the macrostructure (texture, specific structure of separate crystallites, etc.) of polycrystalline diamond films and also to the appearance in them of nondiamond carbon microinclusions at high  $T_c$ .

The analogous character of the temperature dependence of conductivity and the effect of  $T_c$  on the conductivity are true, on the whole, for the longitudinal conductivity of fine-grained polycrys-

talline diamond films, grown on diamond monocrystals from a methane-hydrogen mixture activated by glow discharge (Fig. 4).

The  $T_c$  effect on the conductivity of synthesized diamond films can be accounted for by assumed band bending  $Y_s$  (Fig. 5) on the interface of the crystallites. It would be natural to suppose that changes of  $T_c$  would lead to changes in the spectrum of the electron states  $E_t$  located at the intergrain boundaries. This, in turn, would result in changes of the  $Y_s$  and  $E_{L,H}$  values, which have been experimentally verified.

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