

Formation of nanostructures on an α -C:H film in the presence of an adsorbate

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Processes occurring on the surface of an α -C:H film in the electric field of a STM tip in the presence of trichloroethylene adsorbate are described. It is found experimentally that nanogrowths form in the tunnel gap as a result of the action of positive electric field pulses on the tip. The formation process exhibits a threshold and it occurs in a narrow range of voltages after the threshold voltage is reached. It is shown on the basis of a quantum-chemical calculation that the growths consist of the final product of a graft polymerization reaction of the adsorbate stimulated by the electric field of the tip. © 1995 American Institute of Physics.

The possibility of atomic-level manipulation on solid surfaces was first demonstrated by Becker *et al.* in 1987 (Ref. 1) as the formation of nanosize protuberances on a Ge (111) surface in the field of the tip of a scanning tunneling microscope (STM). In the following years, the fundamental investigation of the atomic-manipulation processes dealt mainly with pure surfaces of several solids, such as gold, silver, and platinum, tungsten and molybdenum chalcogenides. Silicon surface (see Refs. 2 and 3 and the references cited there) in an ultrahigh vacuum was studied most thoroughly. At the same time, the desire to simplify the technological conditions made it necessary to search for a possibility of performing atomic manipulation on a surface in a gaseous or liquid medium. This led to the publication of papers demonstrating the first successful attempts to produce single nanosize growths on the surface of highly oriented pyrolytic carbon from liquid⁴ and gas^{5–7} media. In those studies it was shown that in all cases growths form in the tunneling gap when the voltage on the STM tip reaches a threshold value in the range 3.5–4.5 V (depending on the system). However, the formation mechanism itself and the atomic composition of the structures formed have not been determined.

The choice of graphite as a working surface, of course, was not accidental. It was connected with two fundamental properties of this solid carbon: good electrical conduction and adequate chemical inertness with respect to many gaseous and liquid media. A serious drawback, however, is its low mechanical strength, which accounted for the

formation of a growth in the tunnel gap as a result of the action of an electric pulse and for the peeling off of the surface layers.^{6,7} The desire to preserve the positive qualities of graphite, improving in the process the mechanical properties, led us to the natural choice of a α -C:H type quasidiamond film as a carrying base for the formation of nanostructures.⁸ This x-ray-amorphous solid carbon is a semiconductor, it retains the inertness characteristic of diamond and graphite with respect to many media, and its strength is close to that of diamond. In contrast to the homogeneous surface of pyrolytic graphite, however, the surface of the film is heterogeneous, because the film itself, as determined by many investigations (see the review in Ref. 9 and the references cited there), is a diamond matrix which is disordered by clusters of a graphite structure with transverse size ranging from 2 to 5 nm embedded in it. As a result, the surface of the film consists of islands of diamond and graphite substructures which have different chemical properties: While there are no dangling bonds on the surface of graphite, such bonds are present on the surface of the diamond component and they are saturated with hydrogen atoms. This seemingly unfavorable circumstance for a film, as compared to the uniformity of the properties of a graphite surface, stimulated the development of a criterion which we used and which is presented below, for the formation of stable nanostructures with controllable properties: The structures must be bound with the surface by strong chemical bonds and they must incorporate the possibility of mass growth, again via the formation of new chemical bonds. From the standpoint of this criterion, the diamond component of the film is more promising because of the potential possibility for the formation of stable C-C bonds with adsorbate molecules under certain conditions. It is obvious that a hydrocarbon molecule with an easily revealed carbon atom should be such an adsorbate. This led to the choice of trichloroethylene C_2HCl_3 (TCE) as a gaseous medium and adsorbate at the same time.

The experimental samples had a trilayer structure which consisted of a substrate (silicon or polychore were usually employed) on which a conducting sublayer — a 100 to 150-nm-thick film of nickel or tungsten or an alloy of indium and tin oxides (ITO) — was deposited. A 4 to 7-nm-thick α -C:H film (referred to as film in the text below) was deposited on the conducting sublayer in a plasma-chemical reaction. Isopropyl alcohol was used as the initial reagent for obtaining the film. After the sample was placed in the microscope, the working chamber was evacuated to residual-gas pressure 0.1–1.0 Torr, after which TCE vapor was introduced. A stable adsorbate phase was achieved by evacuating the vapor. The STM tip was then placed at the distance of the tunneling gap to the surface of the sample (the tunneling current was equal to 0.6 nA) and the system was subjected to a series of voltage pulses applied to the sample. The amplitude of the pulses was 1–15 V, the pulse duration was 0.2–10 μ s, and the intervals between the pulses were 2 ms. This regime made it possible to achieve action on the sample with a constant gap between the tip and the substrate. The patterns of the relief obtained with such action are shown in Figs. 1a and 1b.

As one can see from Fig. 1a, growths whose width and height are equal to 6–30 and 3–5 nm, respectively, are formed on the surface of the film under the action of a series of electric-field pulses with a fixed position of the STM tip. The shapes of the growths are stable but the growths appear only when a negative voltage is applied to the sample. The growths appear in a threshold manner at the voltage pulse amplitude $U_{th} = -(2.5-3.5)$

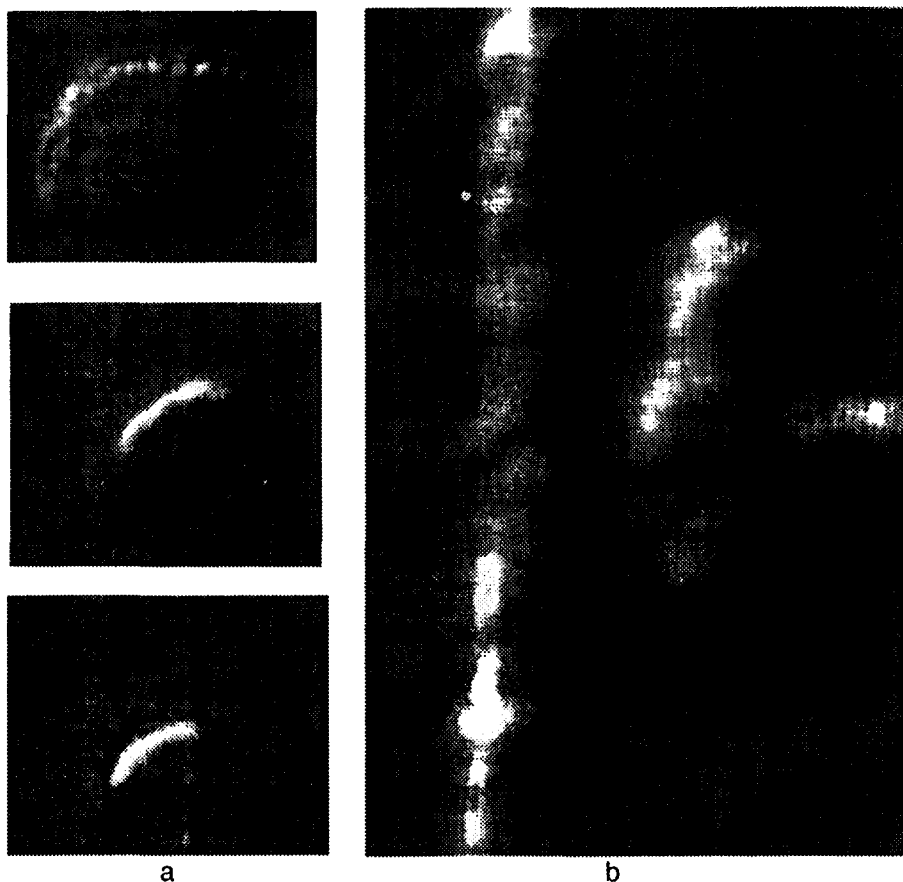


FIG. 1. Pattern of the surface relief of an α -C:H film after the action of electric-field pulses: a — “point-like” action, b — action along a prescribed trajectory.

V. The linear dimensions of the growths are sensitive to the voltage amplitude and the temporal parameters of the pulses only near threshold. For $U \approx 1.51|U_{th}|$ the height and linear dimensions of the growths are virtually independent of the pulse amplitude, the number of pulses in the series, and the pulse duration. This indicates that the main growth formation process occurs in a comparatively narrow range of working voltages. Repeated scanning of the formed structure with scanning voltage $U_{sc} = -0.14$ V on the sample, and also the action of 1–15 V electric field pulses of opposite polarity on the growths does not change their structure. The formation of the growths is an adequately reproducible process, as a result of which it is possible to produce long chains and other geometric figures on the surface along the prescribed trajectories (see Fig. 1b).

The main characteristics of the growths described above show that they are rigidly bound to the surface of the film by stable atomic formations, formed as a result of a chemical reaction between the adsorbate and the film in the presence of an electric field.

It is natural, therefore, that controllable and monitorable formation of these structures depends on how well the type and mechanism of the corresponding reaction is understood. This raised the problem of quantum-chemical modeling of the possible processes in the system TCE — α -C:H in the presence of an electric field. We recently made the first successful attempts to solve such problems¹⁰ with the help of the DYQUAFIELD computational programs,¹¹ which were developed for determining the structure and properties of nanosize atomic systems in electric fields of arbitrary configuration on the basis of modern semiempirical AM1 and NDDO methods, which are close to *ab initio* methods. This system of programs was also used by us. The calculations were performed on a personal computer with a Pentium-90 processor.

The α -C:H film was modeled by a cluster of 207 atoms. This cluster in turn consists of subclusters which combine carbon atoms in sp^2 (graphite) and sp^3 (diamond) configurations in accordance with Robertson's model.¹² It was shown that the graphite and diamond components largely retain their individuality in a cluster. As a result, upon taking into account their considerable length at the atomic level and the well-defined localization of the covalent bonds formed by the carbon atoms, specifically, the C–C bond, we can separately analyze the interaction of the TCE molecules with each component of the film. Accordingly, the interaction of the film with the adsorbate was modeled separately for graphite and diamond components, which were separated from the initial cluster and which consist of subclusters of 56 and 94 atoms, respectively. The electric field is fixed by a collection of point charges, whose arrangement in each case corresponds to the positions of the tungsten atoms in the (111) plane. The calculation was performed in the "dull" tip configuration, in which the area occupied by the point charges covered the area of the transverse section of the cluster under study, which corresponded to the experimental situation with a ~ 10 -nm tungsten tip.

Calculations performed in order to find the atomic configuration corresponding to the minimum of the total electronic energy showed that the reaction leading to rigid bonding of the TCE molecules with the film occurs, as was assumed, only on the surface of the diamond component. The application of strong electric fields has virtually no effect on the high chemical stability of graphite with respect to TCE. The reaction on the surface of the diamond component is stimulated by the field and proceeds only in the case of a negatively charged surface, in complete agreement with experiment. The reaction exhibits a threshold and occurs when the field intensity reaches 5.6 V/nm, but then it again ceases in a field of 8.2 V/nm, consistent with the experimental data. The intermediate reaction products, determined by intermediate iterations in the process of total optimization of the structure, are the radical $C_2HCl_2^*$, a chlorine atom, and a hydrogen atom, removed from the surface (see Fig. 2a). The final result, which corresponds to total optimization of the structure obtained by us, is a strong complex consisting of the radical $C_2HCl_2^*$ and the surface, which are bound by a single C–C chemical bond, and a HCl molecule (Fig. 2b). This complex is not destroyed when an electric field with intensity equal to or greater than the threshold value but with a different polarity is applied to it.

The electric-field-stimulated formation of the C–C bond makes it possible to understand how the bonding of the observed growth with the surface occurs, but it does not explain how the mass of the growth increases. It was found during the modeling process that the mass increase is determined by chemical processes which are stimulated by an

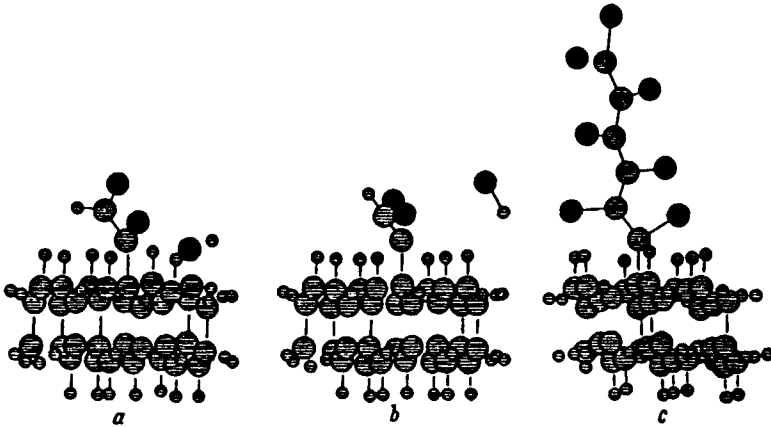


FIG. 2. Behavior of TCE molecules on the surface of the diamond component of an α -C:H film in an electric field of intensity 5.6 V/nm with a positively-charged tip (top): a — start of the molecule-surface bonding stage, b — end of the bonding stage — completely optimized structure, c — formation of a polymer chain.

electric field in the gas medium consisting of TCE molecules near the surface of the film. For example, in calculating clusters consisting of free TCE molecules, it was shown that for the same values of the working voltages as for the above-described reaction free radicals $C_2HCl_2^*$ are formed in the adsorbate system as a result of the direct action of the field and as a result of the initial field-stimulated formation of an ion-radical. It is logical to assume that these radicals initiate polymerization of the adsorbate at the locations where the above-indicated complex is formed (Fig. 2b). As a result, a grafted polymer is formed. One possible configuration of such a polymer is shown in Fig. 2c. The polymerization reaction is nonactivational and occurs within a time shorter than the duration of the experimental pulse.

The systematic features of the field-stimulated and field-maintained radical (ion-radical) grafted polymerization reaction which were studied above correspond completely to the qualitative characteristics of the experimentally formed growths. This correspondence shows that this process is the main mechanism which controls the formation and mass increase of the growths and it makes it possible to propose a reliable algorithm for controlling these processes.

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