Modeling of the role of atomic hydrogen in heat transfer during hot filament assisted deposition of diamond

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The temperature and atomic hydrogen concentration profiles in a hot filament type diamond deposition reactor were determined experimentally and theoretically to demonstrate that the reaction of atomic hydrogen on the substrate surface plays an important role in the heating of the substrate. For a given filament temperature, the substrate temperature in helium was significantly lower than that in either pure hydrogen or 1% methane-hydrogen atmospheres. The presence of small amounts of methane in hydrogen did not have any significant effect in influencing the shape of the atomic hydrogen concentration profile. In the space between the filament and the substrate, the concentration field is established mainly due to the diffusive mixing of the atomic hydrogen with the molecular hydrogen and other species in the gas phase. Homogeneous chemical reactions in the gas phase do not significantly affect the atomic hydrogen concentration distribution in this region.

INTRODUCTION

The importance of atomic hydrogen in the formation of good quality diamond films at low pressures is now well recognized. In most of the low pressure diamond deposition techniques, molecular hydrogen is used in abundance in the feed gas to generate significant amounts of atomic hydrogen in the reactor. Various roles of atomic hydrogen have been indicated. Derjaguin and co-workers suggested that hydrogen is useful both in achieving high diamond growth rates and in reducing graphitic deposits. The ability of hydrogen atoms to preferentially etch nondiamond carbon is thought to assist in the formation of thermodynamically metastable diamond instead of graphite. In a typical hot filament reactor, the concentration of atomic hydrogen near the filament is significantly more than the concentrations of the hydrocarbon species. Away from the filament, the atomic hydrogen mixes with the molecular hydrogen and other gases. Atomic hydrogen also reacts with hydrocarbons to form species such as CH₃ and C₂H₂. The products are considered important for the diamond deposition. Although some atomic hydrogen is consumed by various reactions, a significant amount of atomic hydrogen reaches the substrate surface. When the hydrogen atoms are bonded to carbon atoms at the growth surface, they stabilize the sp³ bonds necessary for the formation of diamond.

In the previous work, the concentrations of atomic hydrogen and hydrocarbon species such as CH₃ and C₂H₂ in the gas phase have been measured by various techniques such as the infrared absorption spectroscopy, the laser induced fluorescence, mass spectroscopy, and catalytic probes. Much of the work was undertaken to develop a better understanding of the gas phase chemistry, gas surface reactions, and the growth mechanism. Although the measurements have provided valuable information about the spatial variation of atomic hydrogen concentration in certain specific systems, the exact shape of the profiles differ with reactor geometry. Apart from homogeneous reactions in the gas phase, mixing of atomic hydrogen with the other species in the gas phase is responsible for the establishment of the species concentration fields. Under typical hot filament reactor operating conditions, the Peclet number for mass transfer is low and the convective mass transport of species is unimportant compared to the diffusive transport. Therefore, the two main factors in the establishment of the atomic hydrogen concentrations in the gas phase are homogeneous chemical reactions of atomic hydrogen and its diffusive mixing with other gases. Knowledge of the relative importance of these two processes is important for modeling of atomic hydrogen concentration profiles for various reactor geometries and operating conditions.

The formation of atomic hydrogen at or near the filament surface is highly endothermic. Atomic hydrogen readily recombines on solid surfaces to form molecular hydrogen and the recombination reaction is highly exothermic. Thus, atomic hydrogen acts as a carrier of heat from the filament to the growth surface. However, none of the previous work was aimed at the investigation of the role of atomic hydrogen in affecting the substrate temperature.

The experimental data analyzed in this paper were obtained from a hot filament chemical vapor deposition (HFCVD) reactor containing a specially designed filament to provide two dimensional symmetry. The design allowed comparison of the experimental data with the model predictions of concentration fields in two dimensions. The computational task involved the solution of a set of partial differential equations representing the conservation of momentum, enthalpy, and concentration of atomic hydrogen. The experimental data on the spatial variation of the atomic hydrogen concentration were compared with the model predictions to examine the appropriateness of calculating atomic hydrogen concentrations by considering only the diffusion and convection phenomena and ignoring consumption of atomic hydrogen due to homogeneous
chemical reactions. To understand the role of atomic hydrogen in substrate heating, the temperatures of a probe, designed to give a measure of the recombination heat and concentration of atomic hydrogen, were recorded as a function of distance from the filament. The extent of substrate heating in helium and hydrogen with and without the addition of a small amount of methane was determined. From the analysis of the data it is demonstrated that the probe temperature can provide reliable measure of the atomic hydrogen concentration profiles.

**PROCEDURES**

To understand the role of atomic hydrogen in heat transfer, experiments were conducted to measure the temperature and atomic hydrogen concentration profiles in a specially designed hot filament reactor. Figure 1 is a schematic diagram of the experimental setup. To achieve two-dimensional symmetry, an inductively heated tantalum ring filament was positioned inside a 50-mm-diam quartz reaction tube. The hydrogen atom probe was constructed with two thermocouples. The tip of one thermocouple was covered with a quartz thimble while the other thermocouple tip was wrapped with a silver wire. The quartz thimble was passivated by rinsing it with ethanol saturated with boric acid and drying. The passivation was designed to minimize hydrogen atom recombination on the quartz thimble. Furthermore, the silver wire provided a catalytic surface for the hydrogen atom recombination. The difference between the temperatures of the two thermocouples should then be a measure of the heat generated by atomic hydrogen recombination and consequently a measure of the local concentration of hydrogen atoms.

In order to determine the temperature and atomic hydrogen concentration profiles, the temperature of the probe at various locations along the axis of the reactor was recorded. Experiments were conducted for a filament temperature of 2473 K, a reactor pressure of 30 Torr, and a gas flow rate of 200 sccm. Temperature measurements were made in hydrogen and helium. Results of several careful experiments indicated that the temperatures were significantly different in hydrogen and helium environments. However, the temperature difference indicated by the two thermocouples in hydrogen was not significantly different from that observed in helium. A careful study of Martin's paper indicated that there are several important reasons why the two thermocouple probe, which worked well for his flow tube experiments, is ineffective for our experiments. First, Martin indicated in his paper that the two thermocouple "probe responds to the hydrogen atom flux through the tube rather than to atomic hydrogen concentration" and that "the temperature difference is linear in atomic hydrogen flux." In Martin's experiments very high gas velocities had to be maintained to achieve a high flux of atomic hydrogen. In our system, the gas velocities used were representative of those typical of hot filament systems which are about two orders of magnitude lower than those used by Martin in his flow tube experiments. At low gas velocities typical of hot filament systems, the flux of atomic hydrogen is much lower and is not sufficient to generate significant differences in the temperatures of the two thermocouples. Second, in Martin's experiments, the thermocouple probe was not located in the direct line of sight of a hot filament heated to 2500 K as in our case. In the presence of a radiation source, the difference between the temperatures of the two thermocouples is diminished thus reducing the sensitivity of the two thermocouple probe. Third, the gas temperatures near the probe in our system are much higher than those encountered in Martin's system. Martin observed that "when the temperature of the flow tube is raised from room temperature to 600 °C, the H-atom signal falls to 0.5 of the room temperature value." Thus, in the presence of an additional heat source such as the convective heat transfer from the gas to the thermocouple, the sensitivity of the two thermocouple probe is severely diminished. In summary the single-gas-two-thermocouple probe is not as accurate as the two-gas-single-thermocouple probe for our experimental conditions.

In all subsequent experiments, the temperatures of a single thermocouple were recorded in pure helium and in hydrogen containing gases. The temperature recorded in helium was taken as a suitable reference for heat transfer due to convection, conduction and radiation from the filament. The temperatures measured in hydrogen, on the other hand, were representative of the heat generated by the recombination of atomic hydrogen at the tip of the thermocouple in addition to the contributions of conduction, convection, and radiation. Since helium is monatomic and no heat of recombination is involved, switching hydrogen with helium provided a credible means of measurement of the reaction heat. Thus, from the temperatures recorded in helium and hydrogen, the recombination heat and hence the atomic hydrogen concentration can be derived.

The heat transfer and fluid flow phenomena in the cy-
lindrical HFCVD reactor are represented by equations of the following form for the conservation of momentum, enthalpy, and concentration of hydrogen atoms.

$$\frac{D}{dx_i} (\rho u_i \phi) = \frac{D}{dx_i} \left( \Gamma \frac{d \phi}{dx_i} \right) + S,$$

(1)

where $\rho$ is the density, $u_i$ is the component of velocity in the $i$ direction, $\phi$ is the dependent variable which can represent velocity components, temperature or concentration of hydrogen atoms, $S$ is the volumetric source term, and $\Gamma$ is the diffusion coefficient which is given an appropriate meaning depending on the variable considered. The details of the specific equations in cylindrical coordinates are described in standard textbooks and are not presented here.

The calculations were performed for a two-dimensional, steady, laminar flow case considering spatial variation of density, viscosity, thermal conductivity, diffusion coefficient, and specific heat. The data used for the calculations are presented in Table I. The input to the model included the size and shape of the reactor and its contents, the thermophysical properties, the rate of supply, and the composition of the input gas mixture and the heating conditions. The velocity, temperature, and atomic hydrogen concentration fields were obtained from the calculations. The boundary conditions included prescription of the input parabolic velocity distribution at the top of the reactor based on the total gas flow rate. The temperature of the inlet gas stream was prescribed to be the room temperature. At the axis of the reactor, the velocity, temperature, and hydrogen atom concentration gradients were taken to be zero on the basis of the symmetry consideration. At the reactor wall, the velocities were assumed to be zero on the basis of the no-slip condition, the temperature was prescribed to be the room temperature, and the hydrogen atom concentration was taken to be negligible. At the exit end, the velocity, temperature, and hydrogen atom concentration fields were assumed to be fully developed. The equations were represented in a finite difference form and solved iteratively on a line-by-line basis. The details of the solution procedure are described elsewhere. A nonuniform grid spacing was used for obtaining maximum advantage in the resolution of variables.

**RESULTS AND DISCUSSION**

Figure 2 shows the variation of probe temperature with distance along the axis of the reactor, in ultrahigh purity helium, hydrogen, and a mixture of 1% methane in hydrogen. The error in temperature measurement was small, with the reproducibility being within ±10°C. In each case, the temperature decreased rapidly with distance from the filament. At any monitoring location, the temperature in helium was significantly lower than that measured in either pure hydrogen or in 1% CH₄-H₂ mixture. Furthermore, when methane was present in the feed gas, the temperature was somewhat lower than that observed in pure hydrogen. Several interesting questions arise from the perusal of the data. Why are the temperatures so different in helium and hydrogen? Can the local concentration of atomic hydrogen be derived from the data? Why does the addition of small quantities of methane affect the temperature?

The temperature and velocity fields, computed for typical diamond deposition conditions, were used to examine the primary mechanisms of heat and mass transfer in the gas phase. In the vicinity of the filament, the velocities were of the order of 25 cm/s, as can be observed from Fig. 3. At these velocities, it takes approximately 40 ms for the species such as CH₂, C₂H₂, and H to travel from the filament to a substrate placed one centimeter away. Since the time constants for the loss of some of these species are of the order of a millisecond, the species cannot be transported to the growth surface by convective mass transport. The relative importance of mass transport by convection and diffusion can be examined with the help of a dimensionless number, the Peclet number for the system. Pe is defined as the ratio of convective mass transport to diffusive mass transfer and is given by $uL/D$, where $u$ is the average velocity, $L$ is a characteristic length, and $D$ is the diffusion coefficient. An order-of-magnitude calculation of the Peclet number for the system yields a value of 0.08 indicating that diffusion, and not convection, is the dominant mechanism of mass transport.

From the temperature field, shown in Fig. 3, it is clear that the temperature profiles are roughly symmetrical.

**TABLE I. Data used for computations.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure, Torr</td>
<td>$P$</td>
<td>30</td>
</tr>
<tr>
<td>Density, gm/cm³</td>
<td>$\rho$</td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity, cal/(cm s K)</td>
<td>$k$</td>
<td>0.8 x 10⁻⁴ + 0.86 x 10⁻⁴ T</td>
</tr>
<tr>
<td>Specific heat, cal/(gm K)</td>
<td>$c_p$</td>
<td>3.34 + 3.4 x 10⁻⁴ T</td>
</tr>
<tr>
<td>Viscosity, poise</td>
<td>$\mu$</td>
<td>2.43 x 10⁻⁶ T⁰.⁶³⁶</td>
</tr>
<tr>
<td>Diffusion coefficient, cm²/s</td>
<td>$D_H$</td>
<td>1346(T)¹.⁷⁵</td>
</tr>
</tbody>
</table>

**FIG. 2.** Probe temperatures recorded in helium, hydrogen, and 1% CH₄-H₂ environments for a filament temperature of 2473 K, reactor pressure of 30 Torr, and a gas flow rate of 200 sccm.
Temperature Field

Velocity Field

1390 K
2473 K
1605 K
1105 K
625 K
410 K

Filament
Quartz Wall

845 K
1390 K
2473 K
1605 K
1105 K
625 K
410 K

2.5 cm
50 cm/sec

FIG. 3. Temperature and velocity fields computed for typical diamond deposition conditions of 2473 K filament temperature, 30 Torr reactor pressure, and 200 sccm gas flow rate.

about the filament. However, a careful examination shows that the profiles are slightly compressed upstream from the filament while the profiles downstream are relatively spread out. This indicates that the gas flow has an insignificant influence on the temperature distribution and that conduction is the primary factor in establishing the temperature field. The ratio of the convective heat transport to conductive heat transport, the Peclet number for heat transfer, is given by \( \frac{\rho u L C_p}{k} \), where \( L \) is a characteristic length for the system, \( u \) is the average velocity, and \( \rho, C_p, \) and \( k \) are the density, specific heat, and the thermal conductivity of the gas, respectively. Under the conditions of this investigation, the Peclet number for heat transfer is of the order of 0.05. The computed temperature field in Fig. 3 is consistent with the low value of the Peclet number and indicates that conduction, and not convection, is the dominant mechanism of heat transfer in the gas phase.

Experiments were conducted to verify the computed temperature profiles. The gas temperatures were derived from the measured thermocouple temperatures by a standard procedure.\(^{17}\) The gas temperatures are derived from the thermocouple temperatures in helium by writing an energy balance at the thermocouple tip for steady state conditions. At the thermocouple tip the radiation heat loss from the thermocouple to the surroundings equals the heat gained by convection from the gas and radiation from the filament. The gas temperature is then given by

\[
T_g = T_t + \frac{1}{h_c} \left( \epsilon_f \sigma v_w T_f^4 - \epsilon_r \sigma v_w T_f^4 \right),
\]

where \( T_g \) is the gas temperature, \( T_t \) is the temperature recorded by the thermocouple, \( T_f \) is the temperature of the filament, \( h_c \) is the convective heat transfer coefficient, \( \epsilon_f \) and \( \epsilon_r \) are the emissivities of the filament and thermocouple, respectively, \( \sigma \) is the Stefan-Boltzmann constant, \( v_f \) and \( v_w \) are the view factors. In order to avoid correction of the thermocouple temperature for heating due to chemical reactions at the thermocouple tip, temperature measurements were made in helium. Figure 4 shows a comparison of the calculated temperatures indicated by the solid line with the experimentally determined values represented by the open circles. It is observed that the computed values are in fairly good agreement with the experimental observations. Thus, the model predictions of the temperature distribution in the reactor are reliable.

The temperatures measured by the thermocouple in hydrogen were significantly different from the temperatures recorded in helium under identical conditions of filament temperature, reactor pressure, and gas flow rate as can be observed from Fig. 2. Since the rate of heat transfer by conduction, convection, and radiation is roughly equal in helium and hydrogen, the above evidence suggests an additional mechanism of heat transport in hydrogen environment. A significant quantity of atomic hydrogen is generated at or near a filament heated in excess of 2000 °C at low pressures. The observation that the power required to heat the filament to a desired temperature in hydrogen was higher than that in helium is consistent with endothermic dissociation of hydrogen. Higher filament power requirements in hydrogen were also reported in previous investigations.\(^{18,19}\) Atomic hydrogen is transported away from the filament primarily by diffusion, as previously established. In the presence of a solid surface, such as the tip of a thermocouple, atomic hydrogen readily recombines to form molecular hydrogen.

\[
\text{H} + \text{H} = \text{H}_2, \quad \Delta H^\circ = -104 \text{ kcal/mole of H}_2.
\]
The recombination reaction is highly exothermic and the energy released heats the substrate. Thus, the endothermic generation of atomic hydrogen at or near the filament and its subsequent transport to the growth surface, where it recombines to form molecular hydrogen, serves as an additional mechanism of heat transport to the substrate. Figure 2 clearly shows that in hydrogen the thermocouple temperatures are higher than the corresponding values in helium by about 400 °C when the thermocouple is placed about a centimeter away from the filament. Thus, in typical hot filament systems where the substrate is placed about 5 to 10 mm away from the filament, the recombination heat plays a major role in substrate heating.

Since the recombination of atomic hydrogen is of significant importance in substrate heating, the spatial variation of atomic hydrogen flux at the substrate surface and therefore, the distribution of the atomic hydrogen concentration in the gas phase, is important for establishing the substrate temperature distribution. Furthermore, the factors responsible for the establishment of the concentration profile in the reactor are also of interest. The local concentrations of atomic hydrogen in the reactor were obtained by solving the equations of conservation of energy for the probe in helium and hydrogen environments. At steady state, the probe energy balance can be expressed as

\[ Q_{\text{rad}} + Q_{\text{conv}} + Q_{\text{chem}} + Q_{\text{cond}} = \frac{d}{dt} (mc_pT) = 0, \]  
where \( Q_{\text{rad}}, Q_{\text{conv}}, Q_{\text{cond}}, \) and \( Q_{\text{chem}} \) are the net heat gains due to radiation, convection, conduction, and chemical reactions, respectively, and \( m, c_p, \) and \( T \) are mass, specific heat, and temperature of the thermocouple tip, respectively. The contributions of radiation, convection, and convection were calculated from the thermocouple temperatures in hydrogen and helium. The specific expressions for the individual terms can be obtained from standard text books. In helium there is no contribution due to chemical reactions. In contrast, the hydrogen atoms are strongly adsorbed at the tip of the thermocouple. Assuming an Eley-Rideal mechanism for the recombination of hydrogen atoms, \( Q_{\text{chem}} \) can be expressed as

\[ Q_{\text{chem}} = -k_f C_H \Delta H^0, \]
where \( k_f \) is the forward reaction rate constant for the recombination of atomic hydrogen, \( C_H \) is the concentration of hydrogen atoms, \( A \) is the area of the thermocouple tip, and \( \Delta H^0 \) is the enthalpy of recombination of hydrogen atoms. An order-of-magnitude calculation indicated that the heat lost by conduction through the thermocouple wires was negligible compared to the heat gained by convection and radiation. Therefore, the conduction heat transfer through the thermocouple wires was ignored in the analysis. Thus, the energy balance for the probe in hydrogen and helium can be expressed by Eqs. (6) and (7), respectively:

\[ A_f \varepsilon \sigma T_f^4 - \varepsilon_{th} \sigma T_{H_2}^4 + h_c A (T_g - T_{H_2}) - k_f C_H \Delta H^0 = 0, \]

\[ A_f \varepsilon \sigma T_f^4 - \varepsilon_{th} \sigma T_{H_2}^4 + h_c A (T_g - T_{H_2}) - k_f C_H \Delta H^0 \]

In order to determine the relative importance of diffusive mixing and homogeneous chemical reactions in determining the concentration profile of atomic hydrogen, computed values of atomic hydrogen concentration profiles were compared with the experimentally derived values. Figure 5 shows the computed concentration profiles of hydrogen atoms in a typical hot filament reactor. The contour values, shown in the figure, represent the local concentrations of atomic hydrogen as fractions of its concentration at the filament. It is observed that in the absence of a substrate, the contours are nearly symmetrical about the filament indicating the importance of diffusive transport of atomic hydrogen. In the calculation of the atomic hydrogen concentrations, homogeneous chemical reactions were assumed to be of negligible importance. If chemical reac-
tions of atomic hydrogen were of significant importance and diffusive mixing was not the only important factor for the establishment of the concentration profile, the computed concentration profile would have been substantially different from the experimentally determined profile. Figure 6 shows a comparison of the experimental and the computed concentration profiles. It is observed that the computed concentration profile is in good agreement with experimental data. Under conditions typical of the HFCVD of diamond, homogeneous chemical reactions do not play a significant role in determining the concentration profile of atomic hydrogen. The diffusive mixing of atomic hydrogen with other gases is the dominant factor in the establishment of the atomic hydrogen concentration profiles.

The addition of small amounts of methane to hydrogen resulted in the lowering of the thermocouple temperature indicating a decrease in the concentration of atomic hydrogen. The change in atomic hydrogen concentration at any particular distance from the filament can be roughly estimated assuming that the rate constant $k_f$ in Eq. (9) does not change significantly upon the addition of methane. Using the data in Fig. 2, the decrease in atomic hydrogen concentration with 1% methane addition was calculated to be about 37% at a distance 10 mm from the filament. Ceill and Butler reported a similar effect of methane addition. Under conditions similar to our experiments, the resonance-enhanced multiphoton ionization (REMPI) intensity of the atomic hydrogen peak, 8 mm from the filament, decreased 33% as a result of the addition of methane. Meier et al. also reported a decrease in the atomic hydrogen concentration with methane addition. However, in their experiments, the filament temperature was not adjusted after methane addition. The changes in the concentration resulted due to a combined effect of changes in (a) filament temperature and (b) gas composition due to methane addition. Unfortunately, their data cannot be used to obtain reliable quantitative effects of methane addition.

If the observed decrease in atomic hydrogen concentration is due to chemical reactions of atomic hydrogen with the hydrocarbon species, the experimentally observed atomic hydrogen concentration profile in a methane-hydrogen gas mixture would deviate from the profile predicted on the basis of diffusive mixing. However, if the generation of atomic hydrogen at the filament is reduced due to the addition of methane and homogeneous chemical reactions do not significantly alter the concentration of atomic hydrogen, good agreement should be achieved between the shapes of the experimental and the computed profiles. It is observed from Fig. 7 that the experimentally determined atomic hydrogen concentration profile in 1% CH$_4$-H$_2$ is in good agreement with the theoretically computed profile ignoring homogeneous chemical reactions of atomic hydrogen. In addition, the power required to heat the filament in a methane-hydrogen gas mixture was lower than that required to heat it in pure hydrogen, indicating a lower rate of generation of atomic hydrogen at the filament in the presence of methane. The presence of small quantities of methane reduces the concentration of atomic hydrogen in the reactor and diffusive mixing continues to be the most important factor in the establishment of the concentration field of atomic hydrogen.

Of the two possible reasons for the lowering of the atomic hydrogen concentration due to methane addition, i.e., possible gas phase reactions of atomic hydrogen and diminished generation of atomic hydrogen at the filament, convincing experimental evidence has been reported in support of the latter argument. In the experiments of Meier et al., after the atomic hydrogen concentration dropped due to methane addition, the gas composition was immediately changed to pure hydrogen. If gas phase reactions were important, the atomic hydrogen concentration would change to its original value prior to methane addition. However, the results demonstrated that the concentration of atomic hydrogen generated from the pure hydrogen feed stream, after withdrawal of methane, was the same as that observed when methane was present. Thus, the nature of
the filament controlled the dissociation of hydrogen and gas phase reactions were not of significant importance. Since the rate of generation of atomic hydrogen is diminished due to a change in the nature of the filament, the addition of a small amount of methane can substantially change the atomic hydrogen concentration in the reactor. Further methane additions will only bring about progressively smaller changes in the atomic hydrogen concentration. The observed decrease in atomic hydrogen concentration in our experiments is in good agreement with the results of previous investigations.5,21

SUMMARY AND CONCLUSIONS

Temperature and atomic hydrogen concentration profiles in a hot filament assisted diamond deposition reactor were determined to understand the role of atomic hydrogen in heat transfer. The results indicate that in a typical hot filament diamond deposition environment, heterogeneous recombination of hydrogen atoms results in significant heating of the substrate. Analysis of the experimental and computed concentration profiles of atomic hydrogen indicate diffusive mixing to be the most important factor in the establishment of its concentration profile. Homogeneous chemical reactions in the gas phase do not have a significant effect on the spatial distribution of atomic hydrogen concentration. Addition of small quantities of methane in the feed gas reduces the rate of generation of atomic hydrogen at the filament. However, the diffusive mixing of atomic hydrogen continues to be the most important factor in determining its concentration profile.

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