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Molecular beam mass spectrometry investigations of low temperature diamond growth using CO_2/CH_4 plasmas

J. Petherbridge, P.W. May*, S.R.J. Pearce, K.N. Rosser, M.N.R. Ashfold

School of Chemistry, University of Bristol, Bristol BS8 1TS, UK

Abstract

Diamond films have been successfully deposited at substrate temperatures as low as 435°C using CO_2/CH_4 gas mixtures in a microwave plasma chemical vapour deposition (CVD) reactor. In order to understand why it is possible to grow diamond at these low temperatures using these gases, we have performed the first in situ molecular beam mass spectrometry studies to measure, simultaneously, the concentrations of the dominant gas phase species present during growth over a wide range of plasma gas mixtures (0–80% CH_4, balance CO_2). Optical emission spectroscopy has also been used to investigate gas phase species present in the microwave plasma. These experimental measurements give further evidence that CH_3 radicals may be the key growth species and suggest that CO may be of greater importance to the plasma chemistry of CO_2/CH_4 gas mixtures than previously thought. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Diamond growth; Low temperature; CO_2-based plasmas; Mass spectrometry

1. Introduction

The outstanding properties of diamond films grown by chemical vapour deposition (CVD) have attracted much interest during recent years [1,2]. Well established conditions for diamond growth include the use of high substrate temperatures (> 700°C) and a carbon-containing precursor gas diluted in excess hydrogen (typically < 5% CH_4 in H_2) [3]. A major goal in the field of diamond CVD is the lowering of substrate temperatures required for growth, as this could permit the use of a much wider range of substrate materials.

Many gas mixtures containing varying ratios of O, C and H have been investigated in the search for a viable low temperature diamond deposition process. In 1991, Bachmann et al. [4,5] collated the results from over 70 such deposition experiments to produce an atomic C–H–O phase diagram for diamond deposition, showing that low pressure synthesis of good quality diamond is only possible within a well defined area close to the H–CO tie line. This indicated that the exact nature of the source gases is unimportant for most diamond CVD processes, and that it is only the relative amounts of C, H and O which govern whether diamond deposition takes place.

The use of CO_2/CH_4 gas mixtures in microwave plasma CVD (MWCVD) has been reported to enable lower temperature growth [6,7]. For low power microwave systems (1–3 kW) the process window for this gas mixture is centred at a composition of 50% CH_4/50% CO_2 by volume flow rate [8,9]. The diamond growth regime begins sharply at 50% CH_4 and at lower CH_4 concentrations no film growth is seen. The boundary for higher CH_4 concentrations is much less

* Corresponding author. Tel.: +44-117-928-9927; fax: +44-117-925-1295.

E-mail address: paul.may@bris.ac.uk (P.W. May).

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well defined, but good quality diamond growth only occurs up to approximately 54% CH_4 — above this non-diamond films are produced. It should be emphasised that these comments apply only to the lower power microwave systems, for which the majority of data are available in the literature. Higher power (> 5 kW) systems operating at a few hundred torr pressure may have a different optimum gas mixture for growth due to differing gas phase chemistries at these increased powers, but there is still little published work on the process window for these systems.

It has been proposed [10] that in these oxygen-containing gas mixtures, O, O_2 and OH species in the plasma perform some of the functions of the H atoms that dominate the gas phase chemistry of more conventional gas mixtures (such as 1% CH_4/99% H_2). These functions are, for example, the etching of non-diamond carbon [8] and the removal of unsaturated hydrocarbons in the gas phase [11]. However, no direct evidence has been presented to support the idea that O, O_2 and OH species are present in sufficient quantities to do these similar tasks.

To date, simple optical emission spectroscopy (OES) studies have been the major diagnostic applied to CO_2/CH_4 plasmas [8,9,12]. Balestrino et al. [12] found a correlation between optimum diamond growth rate (and quality) and the ratio of the emission intensities from CH (431 nm) and C_2 (505–517 nm), and suggested this as a practical gauge to optimise growth conditions for unfamiliar gas mixtures. Later, Mollart and Lewis [8] found that the ratio of the H_α (656 nm) and C_2 emission peaks varied with gas composition, but that this ratio had only a weak correlation with the diamond deposition domain. Subsequently, OES studies in our own group [9] involving a wide range of gas mixing ratios (0–60% CH_4) showed that maxima in the emission intensity ratios of CH/C_2, H/C_2 and CH/C_3 could all be used as indicators for optimal diamond growth conditions. We also found that at > 55% CH_4 the plasma produced significant amounts of soot, which caused a rising background in the OES spectra at longer wavelengths (> 500 nm). This background was attributed to black body emission from soot particles in thermal equilibrium with the gases in the plasma region. Fitting this background curve to the Planck distribution function allowed an estimate (~ 2000 K) of the plasma temperature.

However OES only detects those gas phase species which emit light. In order to understand fully the chemistry of these new gas mixtures, measurements of non-emitting species are also necessary. Itoh and Matsumoto [13] used basic mass spectroscopy of a low power quartz-discharge-tube plasma using $CO_2/CH_4/Ar$ mixtures to measure the concentrations of some of the gas phase species, but only a single gas mixture was investigated. The present work uses the much more powerful technique of in situ molecular beam mass spectrometry (MBMS) to detect simultaneously both stable species and more reactive entities, such as radicals. Hsu [14] originally used MBMS to investigate MWCVD using CH_4/H_2 gas mixtures, sampling the gas via an orifice in the substrate to allow analysis of the composition of the flux incident to the diamond growing surface. Later work in our group used MBMS to sample gas directly from the plasma, thus probing the gas phase chemistry in isolation, with minimum perturbation from gas-surface reactions. This technique has been used to obtain absolute mole fractions of gas phase species present in both hot filament [15–18] and microwave systems [19,20].

We now report the results of the first MBMS study of MWCVD using CO_2/CH_4 gas mixtures over a wide range of plasma compositions (0–80% CH_4), in which all the important gas phase species are monitored.

2. Experimental

2.1. Growth experiments.

Diamond deposition was carried out using a 1.5-kW ASTeX-style 2.45 GHz microwave plasma CVD reactor. The chamber was water-cooled and contained a water-cooled Mo substrate holder. By varying the water flow rate and using steel spacers placed between the cooling coil and the substrate holder, it was possible to achieve and control substrate temperatures in the range of 435–845°C.

The substrate temperature was monitored via a K-type thermocouple (TC1) clamped into a hole that had been drilled into the underside of the substrate holder (~ 1 mm from the platen surface). Calibration experiments were performed enabling this thermocouple temperature reading to be scaled to give an accurate value of the true temperature of the substrate surface. The calibration was performed in two stages, over two different temperature ranges. For substrate temperatures below 600°C, a second K-type thermocouple (TC2) was clamped directly onto the surface of a Si substrate sitting on the substrate holder within the reaction chamber. An electric heater element was then placed ~ 5 mm above the substrate and the chamber was filled with a 50% CO_2/50% CH_4 gas mixture at a pressure of 40 torr. Comparison of the true substrate temperature from TC2 with the temperature reading from TC1 allowed calibration of the latter. Calibration measurements for substrate temperatures above 600°C were performed with the plasma ignited, using a 2-colour optical pyrometer. Extrapolation of the calibration curve from the low temperature experiments into the high temperature region produced a pleasing overlap of the two curves, allowing TC1 to be used to give an

accurate measure of the true substrate temperature in all subsequent experiments.

Feedstock gas flows of CH_4 (99.999%) and CO_2 (99.99%) were regulated by mass flow controllers, thus allowing mixtures to be simply defined as %CH_4 (= 100% CO_2) by flow rate, with total gas flow rate remaining constant at 80 sccm.

Films were deposited on ~2 cm^2 single crystal (100) silicon wafers, manually pre-abraded with 1–3 μm diamond grit. The duration of deposition was 8 h at a pressure of 40 torr and 1 kW applied microwave power. All deposition runs reported here used a feedstock gas mixture of 50% CO_2/50% CH_4, while MBMS experiments used gas mixtures containing various ratios of CH_4 and CO_2.

Films were examined using scanning electron microscopy (SEM) to determine crystal morphology and thickness, and by 514.5 nm (Ar^+) laser Raman spectroscopy (LRS) for film quality.

2.2. Optical emission spectroscopy

Optical emission spectra were collected using an Oriel InstaSpec IV spectrometer. The emission from the plasma exiting through a quartz viewport was focused onto a quartz fibre-optic bundle. Light was sampled from the centre of the plasma ball with a spatial resolution of ~3 mm, and dispersed using a diffraction grating onto a CCD array detector giving a resolution better than 0.3 nm. Emission spectra were obtained for the wavelength window 200–520 nm using the same conditions used for deposition experiments, except with varying gas mixing ratios.

2.3. Molecular beam mass spectrometry

A full description of the MBMS system and gas sampling technique has been published previously [19], but a brief outline will be given here. A two stage differential pumping system was used to sample gas (at 40 torr) from the side of the microwave plasma ball via an orifice (~100 μm diameter) in a molybdenum sampling cone. Gas passing through the orifice experienced a pressure differential ($40 \rightarrow 10^{-3}$ torr) and underwent adiabatic expansion forming a molecular beam in which chemical reactions were effectively frozen out. The molecular beam then passed through a collimating skimmer into the quadrupole mass spectrometer (Hiden Instruments) maintained at ~10^{-6} torr. Species entering the mass spectrometer were ionised by electron impact using an electron ionisation energy of 18 eV.

All MBMS measurements were made under the same conditions as the deposition runs, except that the gas mixing ratio was varied and the applied microwave power was increased to 1.2 kW. This was because the presence of the sampling probe reduced the stability of the plasma at 40 Torr, making a higher applied power necessary in order to maintain a stable plasma at this pressure. The temperature of the substrate holder during MBMS measurements varied from ~450°C for a pure CO_2 plasma to ~400°C at high %CH_4.

Unlike previous work using CH_4/H_2 plasmas [15,19,20], it has proved impossible to convert the counts measured by the MBMS into absolute mole fractions. This is because, when using CH_4/CO_2 plasmas, there is no way of doing an absolute calibration for all of the detected species. For this, we would need to know, first, the thermal diffusion coefficients for species of different masses within the plasma bulk, second, the transmission efficiency of the sampling orifice to heavy and light particles, and finally, the sensitivity factors for the detector to different species. Although estimates for some of these data can be obtained, we lack sufficient information about all of the important species to make conversion of counts into absolute mole fractions reliable. Therefore, no correction has been made for thermal diffusion effects, which may result in the experiment being more sensitive to lighter species (e.g. H_2) than heavier species (e.g. CO_2). As a result, no quantitative comparisons of species counts detected will be made, and the quoted magnitudes of signal counts should be treated with caution. Instead, this work will be restricted to comparing the trends observed in species counts over the range of plasma gas mixtures investigated.

3. Results and discussion

3.1. Film deposition results

Fig. 1 shows the crystallinity and facet size for films grown at various substrate temperatures. At 435°C (a) the deposit is made up of a barely continuous film of rounded particles. A second layer of isolated rounded particles is beginning to form on top of the first layer, but appears to be poorly adhered. At 590°C (b) and 650°C (c) a continuous film is obtained with poorly defined crystal facets which improve in crystallinity with increasing temperature. At 845°C (d) a continuous film with well-defined, crystalline facets is obtained. The (111) diamond crystal plane is prominent in all the continuous crystalline films. Fig. 2 shows the variation of film growth rate and Raman spectra with substrate temperature. Film growth rate is seen to rise exponentially with increased substrate temperature (see Fig. 2a). Fig. 2b shows a decrease in the FWHM of the diamond Raman peak (1333 cm^{-1}) with increasing substrate temperature indicating an increase in the quality of diamond. The height of the diamond peak relative to the graphitic G band at ~1550 cm^{-1} also increases with increasing temperature, indicative of a

reduction in sp^2-bonded carbon content in the films. As the substrate temperature was controlled independently from other conditions the observed decrease in crystallinity, quality and growth rate with lowered substrate temperature is likely to be due to the reduced efficiency of surface reaction(s).

3.2. Optical emission spectroscopy

Fig. 3 shows OES spectra for three different gas compositions. The spectrum of a 20% CH_4/80% CO_2 microwave plasma (Fig. 3a) is dominated by intense OH (A–X) emission at approximately 315 nm, but other emissions due to CO, OH and H_β can also be seen clearly. Fig. 3b shows the OES spectrum for a 50% CH_4/50% CO_2 plasma, the optimal gas mixture for growth of good quality diamond. Emission from OH (282 and 308 nm) is now dramatically reduced in intensity, and no longer obscures the 3rd positive and 5B bands (260–370 nm) of CO. Emissions due to C_2 (Swan band 460–480 nm and 500–515 nm) and CH (431 nm) are also seen. A broad emission feature centred at ~ 400 nm is due to C_3 radicals. The OES spectrum from an 80% CH_4/20% CO_2 plasma (Fig. 3c) is domi-

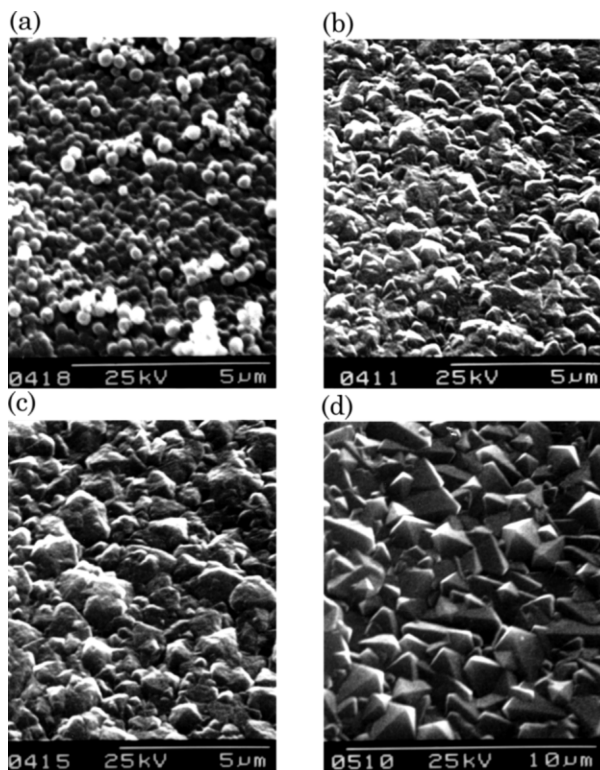

Fig. 1. Electron micrographs illustrating the increase in film crystallinity and facet size obtained with increasing substrate temperature in 50% CH_4/50% CO_2 plasmas. Conditions: 1 kW applied microwave power; total gas flow 80 sccm; pressure 40 torr; growth time 8 h. Substrate temperature: (a) 435°C; (b) 590°C; (c) 650°C; (d) 845°C.

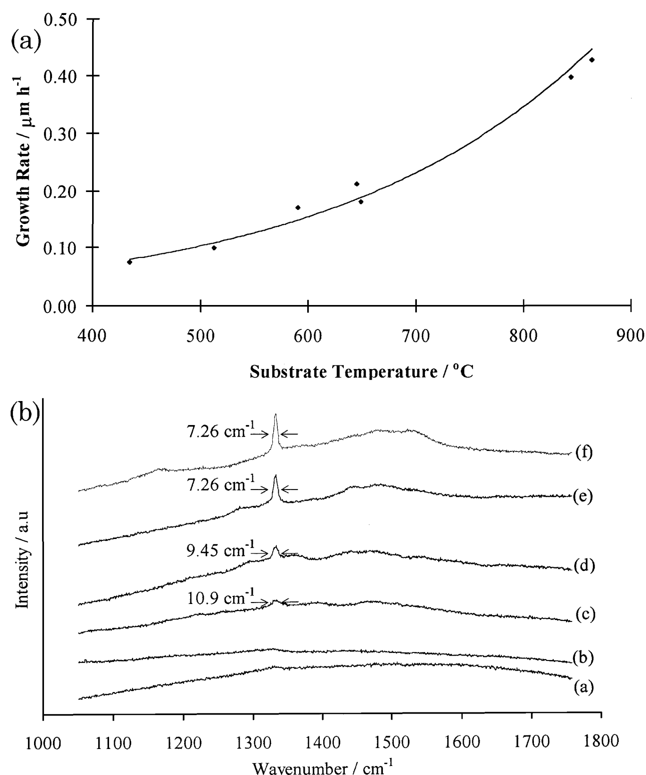

Fig. 2. (a) Film growth rate vs. substrate temperature for films grown in 50% CO_2/50% CH_4 plasmas. The line is a least squares fit to an exponential function. (b) Raman spectra (514.5 nm excitation) of films grown in a 50% CO_2/50% CH_4 mixture at the following substrate temperatures: (a) 435°C; (b) 512°C; (c) 590°C; (d) 650°C; (e) 845°C; (f) 865°C, other conditions as given in Fig. 1. The spectra are each offset vertically for clarity, and FWHM values for the diamond peak at 1332 cm^{-1} are shown on each plot.

nated by C_2 emission, whilst CO and CH emissions are now smaller relative to the increased C_3 feature.

3.3. Molecular beam mass spectrometry

Fig. 4 shows MBMS counts as measured for a number of species, vs. the composition of the plasma (%CH_4). The absolute magnitudes of the counts should be ignored, as the relative sensitivities of the mass spectrometer to each of the species is unknown. However, the relative trends of each species are valid. The CO_2 counts fall from an initial high value at 0% CH_4/100% CO_2 to zero at 40% CH_4. This result is interesting because it shows that all CO_2 is consumed within the plasma for an input gas mixture containing ≤ 60% CO_2. CO and H_2O follow similar trends, both peaking at 20% CH_4 before steadily falling off with increasing CH_4. C_2H_2 only appears above background noise for gas mixtures over 50% CH_4, and thereafter increases steadily. H_2 counts rise with increased %CH_4 before levelling out at approximately 60% CH_4. Care should be taken when considering the measurements

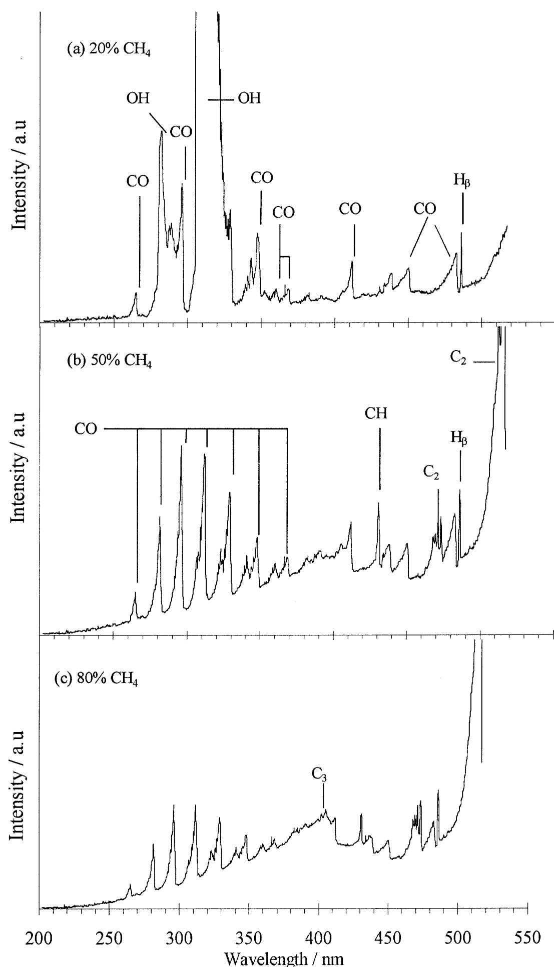

Fig. 3. (a) OES spectra of plasmas involving (a) 20% CH_4/80% CO_2, (b) 50% CH_4/50% CO_2, and (c) 80% CH_4/20% CO_2, other conditions as given in Fig. 1. Note: the response of the CCD detector was more sensitive to longer wavelengths. No correction has been made for this and therefore absolute intensities should be regarded with caution.

made of H_2 because the low mass of this molecule leads to a large scatter in experimental data. Fig. 4b shows data for CH_3 and CH_4 plotted on an expanded vertical scale for clarity. Interestingly, counts for these two species remain at background levels for low %CH_4, and only reach significant levels beyond 40% CH_4. CH_3 counts peak at 50% CH_4 whereas CH_4 counts reach a peak at 56% CH_4. The peak in CH_3 counts is seen to coincide very closely with the gas mixture at which the optimum diamond film growth rate and quality is obtained [8]. It should also be noted that the counts of CH_3 and CH_4 are in general an order of magnitude lower than the other species measured. No significant counts were obtained for O_2, O or OH, despite the strong optical emission from the latter. This again reinforces the fact that intense optical emission is not necessarily a measure of absolute species concentration. Also, counts for C_2H_6 or higher hydrocarbons (e.g. C_3, C_4 species, etc.), were absent, even at very high CH_4%, which is somewhat surprising, given the high levels of soot deposition seen in high CH_4% plasmas.

4. Conclusions

Two important questions arise from this work. What species or chemistry within these CH_4/CO_2 plasmas enables lower temperature growth, compared to that found in the more conventional H_2/CH_4 gas mixtures? And what is the likely growth species? For the first question, since negligible O, O_2 or OH were detected in these plasmas under optimal growth conditions, the conventional idea [8,10,11] that these species are critical for low temperature growth, may need to be revised. The high levels of CO present in the plasma, observed experimentally at the optimum growth mixture of 50% CH_4/50% CO_2, suggest that this species may be more important to the gas-surface interactions than has previously been believed, and may well be a controlling factor for low temperature growth.

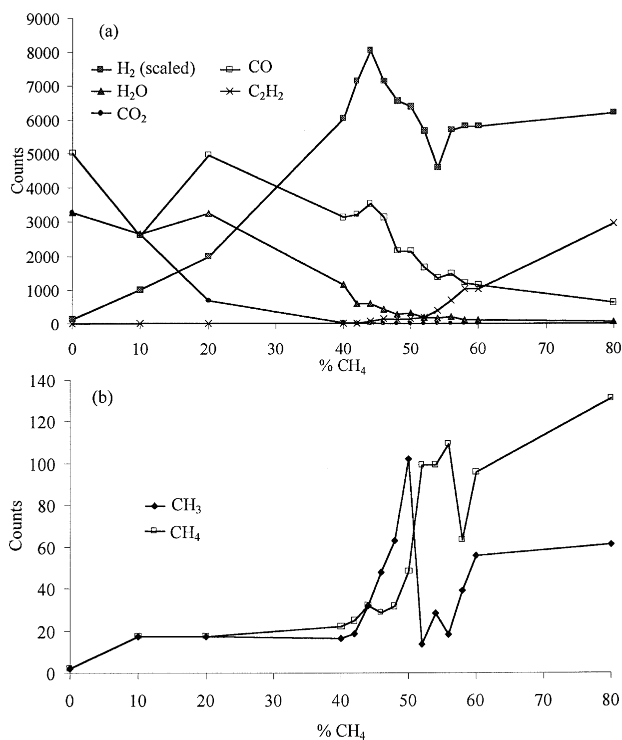

Fig. 4. MBMS plots of species counts vs. %CH_4 in a CO_2/CH_4 gas mixture. The data for H_2 have been reduced by a factor of 40 to fit onto the vertical scale. Conditions as given in Fig. 1, except applied microwave power increased to 1.2 kW to improve plasma stability. For clarity, species with relatively large counts have been plotted in (a), whilst those with low counts are shown on an enlarged scale in (b).

For the second question, the fact that the growth window is so sharp (confined within the range of 50–52% CH_4 for good quality diamond [8,9]), coupled with the results from Fig. 4 which show that the only species whose concentrations change dramatically in this small range are CH_3 and CH_4, strongly suggest that methyl is the growth species (as concluded for CH_4/H_2 processes by Goodwin and Butler [21]). This indicates that the step which propagates the diamond lattice is identical in both CH_4/CO_2 plasmas and various conventional CH_4/H_2 processes, namely the addition of CH_3 to an activated surface radical site [22,23]. Therefore, the difference between the two chemistries arises from the way in which the surface is activated. For CH_4/H_2 mixtures, it is generally accepted that H atoms activate the surface by abstracting a terminating H leaving a 'dangling bond'. Our results now suggest that another species, possibly CO, may perform a similar activation in these CH_4/CO_2 systems.

To conclude—CO_2/CH_4 microwave plasmas show promise for the deposition of high quality diamond films at lower substrate temperatures. Insight into plasma chemistry has been gained by using both OES and MBMS techniques. Further work will involve probing of plasma chemistry by absorption spectroscopy and detailed computer modelling of the gas phase reactions to compare with our measurements. These data will be presented elsewhere [24].

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