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Organic coatings from acetylene at atmospheric pressure: UV light versus plasma

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A versatile pilot-scale reactor has been designed in such a way that it can be readily converted from a dielectric barrier discharge (DBD) "PECVD" operating mode into a photo-initiated "PICVD" one; in the latter, low-pressure mercury (Hg) lamps replace the high-voltage glow discharge plasma. Both processes operate at ambient temperature and atmospheric pressure, 100 kPa, using acetylene (C_2H_2) monomer. In both sets of experiments, it was found that efficient gas-to-solid conversion can occur, in the form of nano-particulate amorphous hydrocarbon polymer-like material. It was found that in the PICVD case very great care was required to exclude even traces of O_2 contamination, because it not only reduced the growth rate of solid, but the latter then became highly oxidized ([O] ~ 50 at.%) and water-soluble.

Keywords: Chemical vapor deposition (CVD); plasma-enhanced (PE); photo-initiated (PI); acetylene; powder

1 INTRODUCTION

Among many methods for depositing thin solid films on solid substrates that have over the years been reported in the literature,^[1] chemical vapor deposition (CVD) plays a key role. In Chapter 6 on CVD of his well-known textbook, Ohring devotes particular subsections to thermal CVD and to plasma-enhanced CVD (PECVD),^[1] but photo-initiated CVD (PICVD) has also been steadily gaining importance thanks to powerful novel light sources like excimer lasers^[2] and UV / VUV lamps.^[3] In PICVD, energetic photons break the covalent chemical bonds of the volatile precursor molecules being used, the energy of which generally calls for wavelengths in the UVC (200-290 nm) or vacuum UV (VUV, < 200 nm) ranges. Regrettably, however, light sources in those wavelength ranges (lasers, or excimer lamps^[3]), even though readily available from numerous international vendors, tend to be quite costly. This applies especially to VUV sources below the cut-off of ultrapure quartz glass, because they must operate with low-pressure chambers, hence additional costly infrastructure. Fortunately, a relatively inexpensive source of UV / VUV radiation has been commercially available since well before the above-named "high-tech" light sources, namely mercury-vapor (Hg) lamps.^[4] Co-authors of this present manuscript have over past years been active in research on both PECVD and PICVD, mostly for depositing organic polymer-like thin films. In the case of PECVD, such so-called "plasma-polymers" (PP) are the object of an enormous body of literature, well-known to the readers of this journal. For the case of organic films generated by PICVD, however, the literature is far less abundant, likely for economic reasons mentioned

above. Hideo Okabe may be considered a "father" of organic VUV photochemistry in the current context, for example considering his often-cited work from the 1960s on VUV photolysis of ethane and propane by hydrogen abstraction.^[5,6] Such photo-induced reactions, and those of other hydrocarbon molecules like acetylene (C₂H₂), object of this present study, yield highly reactive radicals, the precursors of solid film formation. In the case of PECVD, these radicals of course result mostly from electron-impact reactions. Indeed, Okabe's book, Photochemistry of small molecules, may be considered the "bible" of the organic PICVD field.^[7] Figure 1(a), adapted from this book, shows the absorption coefficient, k (log scale) of C₂H₂: Spanning part of the VUV range, $120 \le \hat{\lambda} \le 200$ nm, vertical lines at the wavelengths of certain commercial lamps clearly illustrate how dramatically k decreases with increasing values of λ . Those lamps, used in the present authors' laboratories, are discussed below and in the Discussion section. Figure 1(b), the emission spectrum of a low-pressure Hg vapor lamp, shows two intense lines at $\lambda = 184.9$ nm (VUV) and 253.7 nm (UVC). Referring to (a), the value of k is appreciable at the former, but becomes negligibly small at the latter. Indeed, Benilan et al. reported a further decrease by four orders of magnitude (from $k \sim 10$ to < 0.01) between $\hat{\lambda} = 184.9$ and 253.7 nm.^[8]

The discovery of solid deposits from C_2H_2 gas goes back quite far in time, both by "PECVD" and "PICVD": In an article entitled "*Cuprene: a historical curiosity along the path to polyacetylene*", Rasmussen [**A**] traces early research that eventually led to the 2000 Nobel prize in chemistry to Shirakawa, MacDiarmid, and Heeger for their work on conjugated organic polymers, for example polyacetylene [**B**]: In 1874 P. and A. Thenard described the solid product from an electric discharge in C_2H_2 as hard, glassy and of dark reddish colour [**C**], while other French researchers in 1910 reported rapid formation of a brown-yellow solid under UV irradiation [**D**]. However, apart from their historical interest, those early studies were not very revealing because they gave little information about the solid product (later generically named "cuprene") beside its visual appearance and the fact that its composition was consistent with that of acetylene gas (i.e., $(C_2H_2)n$). One of the early modern reports on organic PICVD was work by Danno and Hanabusa,[9] who used the VUV emission from a Hg lamp [Figure 1(b)] to photolyze pure C_2H_2 feed gas at reduced pressure, p = 400 Pa, in order to deposit amorphous hydrogenated carbon (a-C:H) films. They found the produced films to be electrically resistive and optically transparent in the infrared, but soft. Compared with films obtained by PECVD, the authors stated that "the presence and acceleration of carbon ions play important roles in determining the physical properties, such as refractive index and hardness"; of course, this is now well documented in the literature on so-called diamond-like carbon (DLC).



Figure 1: (a) UV / VUV Absorption spectrum of acetylene, adapted from Okabe.^[7];
(b) Emission spectrum of a low-pressure Hg lamp (adapted from https://www.crystec.com/senlampe.htm)

PICVD has also more recently been investigated by K.K. Gleason and coworkers at MIT, and by S. Girshick's group at the University of Minnesota. O'Shaughnessy *et al.*^[10] reported photodeposition of poly(cyclohexyl methacrylate) thin films on silicon (Si) substrates at $\lambda = 254$ and 365 nm in the presence of benzophenone as photo-initiator. Beside successfully photopolymerizing the cyclohexyl methacrylate monomer, they were also able to demonstrate its controllably micro-patterned deposition. Zhang *et al.*^[11] reported growing up to 20 nm thin poly(methyl methacrylate) (PMMA) coatings on NaCl nanoparticles at ambient pressure and temperature by irradiating monomer vapor with a Xe₂* excimer lamp at $\lambda = 172$ nm. Regarding the set of three VUV sources used in the present authors' laboratories, these were always operated with gaseous reagents under partial vacuum in small, lab-scale reactors, like Kasparek *et al.* described for the case of C_2H_2 .^[12] In other cases, the feed gases were usually ethylene (C_2H_4) and methane (CH_4),^[13-15] although other hydrocarbons also tend to absorb strongly below 200 nm, as does C_2H_2 .^[7] Light hydrocarbon "monomers" were often mixed with a second VUV-absorbing gas, for example NH_3 ,^[13-15] or H_2S ,^[12] in order to prepare amine- or thiol-functionalized coatings for various uses. In some instances, physico-chemical properties of PICVD and PECVD films prepared from the same gas mixtures were compared,^[16,17] including O-rich deposits from C_2H_4 mixtures with O_2 , N_2O and CO_2 ,^[17] all of which absorb strongly at VUV wavelengths below about 160 nm.^[7] By way of example, VUV PICVD greatly outperformed PECVD in creating desired high [NH_2]/[N] values, the fraction of nitrogen incorporated as [NH_2] in coatings from C_2H_4 or CH_4 / NH_3 mixtures, namely up to 75% vs merely ca. 30%.^[15] High concentrations of reactive primary amines, [NH_2], are of advantage in numerous applications, for example in bio-medical ones.^[18]

Clearly, therefore, PICVD can be a desirable, potentially cost-effective and up-scalable technique to generate polymer-like coatings, even at atmospheric pressure. Based on existing literature, it is challenging to compare UV light with plasma for polymerizing any given precursor; indeed, both methods depend very greatly on experimental conditions and on reactor design. Furthermore, it is evident that the same precursor under comparable experimental conditions will likely not yield the "same" polymer-like film. In light of this, the purpose of this present research has been to prepare and compare thin organic coatings from C_2H_2 by PI- and PECVD, in a "pilot-scale" atmospheric-pressure reactor system capable of being readily converted from photo- to plasma-operating modes. A strong motivation has been operating at 100 kPa, thereby obviating the need for vacuum equipment and potentially lowering costs, as already mentioned. This study also investigates the effect of a filter that removes acetone traces coming from the acetylene gas cylinder feeding the reactors. Clearly, all this is unprecedented by earlier literature, differing from the work of Danno *et al.*^[9] by the higher pressure and comparison with PECVD under nominally similar operating conditions.

2 EXPERIMENTAL SECTION

Figure 2(a) presents a scale drawing of the dielectric barrier discharge (DBD) plasma reactor used for PECVD of C₂H₂-based plasma polymer (PP) films.^[19,20] Placed inside a Plexiglass (PMMA) box that is made leak-tight so as to maintain the process gas free from contamination by atmospheric air, it comprises high-voltage (HV) electrodes, polished aluminum plates ($180 \times 60 \times 1.75 \text{ mm}^3$) (**A**); the top (3.50 mm thick MacorTM, **B**) and bottom (3.00 mm thick glass, **C**) dielectric barriers. The lower, moveable grounded electrode platen (**D**) allows one to simulate continuous "roll-to-roll" deposition by back-and forth motion. The discharge gap, (**E**), between (**B**) and (**C**) is typically 2 mm. The feed gas injector is also fabricated from machinable ceramic (MacorTM, **F**). This 240 × 30 × 12.7 mm³ gas diffuser has, on its bottom, 22 holes ($\emptyset = 3 \text{ mm}$) that permit homogeneous distribution of the feed gas across the ca. 20 cm width of the movable substrate. Let us add that an earlier version of this same reactor apparatus used a single cylindrical, ceramic-coated HV electrode that created a roughly 1 cm-long DBD plasma, other geometrical and process conditions being quite comparable. We shall later refer to certain results obtained with that predecessor apparatus [**F**].

Because the current apparatus and experimental procedure have already been described in detail elsewhere,^[19,20] we shall repeat here only the most important aspects. All PECVD experiments were carried out using DBD plasma sustained by audio-frequency high voltage (HV) at f = 20 kHz, $V_a(f) = 2.8$ kV_{rms} (= 8 kV_{pp}, peak-to-peak), using 10 standard liters per minute (slm) of argon (Ar) as carrier gas (99.9+% purity, Air Liquide Canada, Ltd). Acetylene "monomer", C₂H₂ (Air Liquide and MEGS), was dissolved in an acetone-filled cylinder, normal safe storage procedure. A purified C₂H₂ feed gas was provided by passage through a commercial filter capsule (Balston 95A-1/4 Acetylene Filter, Parker, Haverhill, MA, USA) attached to the cylinder outlet, in which active carbon trapped traces of acetone vapor. Some of the experiments were carried out in absence of the filter, to investigate the effect of acetone on resulting plasma polymers. C₂H₂ at concentration in the few ‰ range was added to the 10 slm Ar carrier flow in



Figure 2: (a) Scale drawing of the PECVD (DBD) reactor: upper electrodes (A); lower electrode (D); dielectric barriers (B, C); discharge gap (2 mm) (E); gas injector / diffuser (F). Reproduced from ref. 19, with permission. (b) Schematic diagram of the PICVD reactor: low-pressure Hg lamps (A); reflectors (B); the other elements are identical to the PECVD configuration. (c) Photographic image of the PICVD reactor in operation.

a mixing chamber placed upstream from the DBD reactor; its flow rate, F_d , was controlled by an electronic mass flow meter. Plots of energy per molecule, E_m , versus monomer flow, F_d , and versus $1/F_d$, in Ar DBD plasmas are presented in Nisol *et al.*^[20] More will be said about this further below.

Regarding the PICVD reactor, **Figure 2(b)**, the PECVD system was readily modified by replacing the upper portion, **A** and **B**, by two commercial low-pressure Hg lamps (212 mm long, model STER-L-RAY[®], from Atlantic Ultraviolet Corp, Hauppauge, NY, USA) as shown by the scale drawing; thanks to the high-purity silica envelope (transparent down to ca. 160 nm), their emission closely resembled that shown in **Figure 1(b)**. Coatings obtained by both PECVD and PICVD techniques, with or without use of the acetylene filter, were deposited on pieces of single-crystal silicon (c-Si) wafer, typically a few cm² in size. Their composition and structure were characterized by X-Ray Photoelectron Spectroscopy (XPS) using a K-Alpha instrument from Thermo Fisher Scientific, with Al K_{α} radiation and a 400 µm spot size. Deconvolution of the high-resolution (HR) C1s peaks was performed with CasaXPS software. Possible solubility of the coatings was assessed by placing a water droplet on their surface, followed by visual inspection. Deposits were also examined by scanning electron microscopy (SEM) using a JSM-7600 TFE field-emission (JEOL, USA) instrument.

For reasons that will be explained later in this text, the PICVD module shown in **Figure 2(b)** was later removed from the Plexiglass box and instead installed in a hermetic glovebox (MBraun, model LABmaster pro) at McGill university,^[12] under ultra-pure Ar atmosphere at 100 kPa in which the total O_2 concentration could be maintained below 1 ppm. Nominally identical PICVD experiments were carried out in both enclosures, the Plexiglass one and the glove box, using 10 sccm flows of pure C_2H_2 for 10-minute durations.

3 RESULTS AND DISCUSSION

3.1 PECVD

We begin by presenting PECVD results obtained in the reactor depicted in Figure 2(a). It is well documented that the principal mechanism of plasma polymerization in dilute Ar / hydrocarbon monomer mixtures is via Penning transfer of energy from metastable excited Ar* and Ar₂* states to the monomer molecules, resulting in their dissociation (formation of precursor radicals). This is discussed for example in the work of Nisol *et al.*,^[20] where the plot of $E_{\rm m}$ versus monomer flow rate $F_{\rm d}$, displays the usual peaked curve, with $(E_{\rm m})_{\rm max} = 11.4 \text{ eV}$, and the slope of $E_{\rm m}$ versus $1/F_{\rm d}$, the power *P* absorbed in the discharge, P = 13.8 W. The maximum, which occurs at $F_{\rm d} \sim 20$ sccm, separates the "monomer-lean" region from the "monomer-rich" one, where plasma polymerization rate, *r*, is higher. In Nisol *et al.*^[19], Fricke et al. [**F**], and here, it was observed that PP layers deposited quite rapidly, but were powdery in nature, due to the well-documented property of C_2H_2 plasmas to form solid nanoparticles in the gas phase.^[21] In a rather extreme example, a 40 min.-long deposition run with $F_d = 40$ sccm resulted in a deposit close to 40 µm in thickness, but of low overall mass density, $\rho = 0.17$ g.cm⁻³, only about 20% of the expected bulk value. In other words, the value of *r* was high, ca. 17 nm.s⁻¹, but it was also found that during the ~ 0.2 s residence time and transit through the active plasma zone, C_2H_2 molecules were near-totally converted to solid form,^[20] presumably on account of extreme reactivity due to breakage of the molecule's triple bond. We shall return to these observations in the Discussion section further below.

In Table 1 are reported XPS analytical results of PP films deposited under various conditions, with and without use of the acetone ("Ac") filter; with $F_d = 10$ sccm we found $r \sim$ 0.4 nm.s⁻¹. The reason for the experiments without filter was to examine how much oxygen might be incorporated into the film structure by possible entrainment of traces of the Ocontaining Ac molecules in the flow of C₂H₂ feed gas. Clearly, inspecting the relevant data in Table 1, this does not appear to have been the case, because the broad-scan XPS oxygen concentrations, [O], were the same, within limits of experimental accuracy, as were highresolution O1s peaks (not shown). What does deserve mention, however, are the relatively high [O] values, on one hand, and the presence of nitrogen in the films, $1.8 \le [N] \le 3.8$ at.%, on the other. In the PP literature, it is well known that trapped radicals rapidly react with O₂ when exposed to atmosphere, but not with N₂ (on account of its high bond energy, ca. 9 eV).^[22,23] Another possible source, as noted earlier, is that the Plexiglass box enclosing the DBD plasma system allowed some air infiltration, despite the constant flow of pure Ar carrier gas. We return to this remark again further below. To summarize, the PECVD experiments yielded PP film deposits of comparable quality to those obtained in our earlier experiments with C2H2 monomer $^{[19,20]}$ in this same reactor, as well as those in its earlier version, [O] = 10.9 \pm 0.2 at.%. [E]

Туре	Acetone Filter	C1s (at%)	N1s (at%)	O1s (at%)
PECVD	Yes	87.5 ± 2.5	2.6 ± 0.8	9.9 ± 1.7
	No	90.8 ± 0.9	1.4 ± 0.5	7.8 ± 0.4
PICVD	Yes	44.8 ± 1.4	0.8 ± 0.2	54.3 ± 1.5
	No	43.9 ± 0.4	1.1 ± 0.1	54.9 ± 0.4
PICVD (Glovebox)	Yes	96.7 ± 0.1	-	3.3 ± 0.1

 Table 1: XPS measurement for 4 samples (+duplicates)

3.2 PICVD

In contrast with PECVD experiments, PICVD needs to be carried out with pure C_2H_2 , not with noble gas-diluted monomer; this was first accomplished in the reactor depicted schematically in **Figure 2(b)**, photographically in **Figure 2(c)**, placed first in the Plexiglass enclosure, then subsequently in the glovebox workstation.^[12] It is noteworthy that no deposition whatever could be observed, unless the Hg lamp had an ultra-high purity quartz-glass envelope. In other words, it is evident that only the 185 nm VUV emission line [see **Figure 1(a)**] contributes to photopolymerization of C_2H_2 . In this case the mechanism for creating precursor radicals is bond scission via photolysis, followed by recombination reactions, as portrayed in Equation (1) to (4) below.^[24-27] The reader is referred to Kasparek *et al.*^[12] for a more detailed discussion:

(i) Direct dissociation:
$$C_2H_2 + hv (> 5.8 \text{ eV}) \rightarrow C_2H \cdot + H \cdot$$
 (1)

(ii) Formation of metastable excited intermediate: $C_2H_2 + hv (> 5.8 \text{ eV}) \rightarrow C_2H_2^*$ (2)

(iii) Excited molecule-mode polymerization:
$$C_2H_2^* + C_2H_2 \rightarrow C_4H_4^*$$
 (3)

$$C_4H_4^* + C_2H_2 \rightarrow C_6H_6^*$$
, etc. (4)

To render experimental conditions between the two (PI- and PE-) CVD techniques as closely comparable as possible, beside the "same" reactor geometry and operation at 100 kPa, we selected the same monomer flow rate, $F_d = 10$ sccm. This value was based on prior optimization experiments considering the molecules' residence time under the UV lamps. Despite this, r values for PICVD were found to be low, typically less than 5 nm.min⁻¹ (0.1 nm.s⁻¹), i.e. < 20% of the PECVD value. For comparison, Danno and Hanabusa cited r values of 50 and 20 nm.hr⁻¹ (0.014 and 0.006 nm.s⁻¹) at 150 and 300 °C, respectively, of course at p = 400 Pa, 250 times lower pressure.^[9] An obvious conclusion based on these data would be that PICVD is a slow process when using C₂H₂ and a Hg lamp as VUV source, in agreement with the absorption spectrum from **Figure 1(a)**. However, the highly unusual XPS analyses of PICVD deposits (namely, the high O-content, **Table 1**) led us to search for alternate explanation:

The nearly constant high value of [O], $53.3 \le [O] \le 56.5$ at.%, with or without the Ac filter indicated that the Plexiglass enclosure could not completely exclude some slight air infiltration, although this could not be measured without suitable specialized instrumentation. In the PECVD case, the constant 10 slm Ar flow provided effective mitigation (see section 3.1), but for PICVD the need for undiluted C₂H₂ feed gas proved to render contamination unavoidable and with the more serious consequences for deposit composition. This occurred despite counterefforts to minimize possible O₂ access into the reaction zone, with a plastic envelope around the PICVD reactor representing a small secondary enclosure within the Plexiglass box. We concluded that even traces of O₂ lead to photo-dissociation into atomic O and resulting etch reactions that compete with PI-deposition of hydrocarbon film. Probable added cause for high [O] is that, like PP deposits, trapped radicals in PICVD hydrocarbon films also strongly react with O₂ when exposed to atmosphere.^[22,23] PP films like the present PECVD ones generally possess cross-linked structures that convey to them low solubility, while their PICVD counterparts disappeared rapidly under a drop of water. Based on the considerations just presented, there existed a strong motivation to repeat the PICVD experiments in the above-mentioned glovebox workstation,^[12] where < 1 ppm of O₂ could be assured. The outcome of this 10 minute, $F_d = 10$ sccm experiment with pure C₂H₂ is illustrated in **Figure 3(a)**, where the yellowish rectangular regions (on the Al foil backing) are a few µm thick VUV-polymerized nanoparticle deposits, apparently much akin to the ones obtained by PECVD (**Figure 3(b**))^[19] already mentioned in section 3.1 above. Unlike in that case, however, the low-density powder layer here grew less rapidly, and its XPS analysis is presented at the very bottom of **Table 1**. **Figure 4 (a,b)** compares SEM images of the powdery PECVD and PICVD deposits that show (**a**) "cauliflower-like"[**E**] and (**b**) near-spherical morphologies, respectively. In **Figure 4(c)**, SEM side- and top-view images of an atmospheric pressure DBD PECVD coating on glass (5 slm of Ar, 40 ‰ of C₂H₂, f = 2 kHz, $V_a = 6$ kV_{PP}) illustrate a compact deposit, with the spheroidal "cauliflower-like" features appearing only at the very top [**E**].

The obvious conclusions to be drawn from the experiments described above are the following: when carrying out PICVD with acetylene as monomer, it is imperative to scrupulously exclude even the slightest traces of contamination from the reaction zone, because O_2 also forms highly reactive species such as ozone under VUV irradiation, species which vigorously react with the organic precursors. The effect of powder formation, well documented for the case of C_2H_2 as reagent gas,^[12,28] can likely be minimized, possibly even suppressed, as illustrated by **Fig.4(c)**, where a transition from a low-density phase to a compact one was clearly visible, even though the mechanism therefor is presently not clear. It is noteworthy, however, that this same phenomenon was also observed in that same study by Fricke et al. for the case of N_2 carrier gas, not only with C_2H_2 , but also the other hydrocarbons they investigated (C_2H_4 , C_2H_6 , CH_4).[**F**] Suppression of powder formation can also be achieved by elevating the substrate temperature during PE- or PICVD, and/or by reducing pressure during PICVD as

reported by Danno and Hanabusa,^[9] These aspects, however, are left for future investigation, as are possible practical applications of the present powdery deposits.



Figure 3: (a) Powdery PICVD layers from $F_d = 10 \operatorname{sccm} C_2H_2$ under the Hg UV lamps (elongated yellowish rectangles; the smaller dark ones are c-Si); deposition time: 10 min. (b) Thick PPA deposit generated in Ar ($F = 10 \operatorname{slm}$)/acetylene ($F_d = 20 \operatorname{sccm}$) DBD plasma at 20 kHz. The applied voltage, V_a , was 2.8 kV_{rms} and the deposition time 10 min. The substrate was stationary during deposition, the grounded electrode platen only being moved afterward for acquisition of this photograph (Reproduced from ref. 19, with permission).



Figure 4: (a) SEM image of a powdery PECVD layer displaying "cauliflower-like" morphology; (b) SEM image of a PICVD layer at somewhat lower magnification, showing near-spherical particles over a continuous film; (c) cross-sectional and top views of a PECVD coating on glass after fracture; the top and side-view bars both correspond to 1 μ m (with permission, from [E]).

4 GENERAL DISCUSSION AND CONCLUSION

In sections 3.1. and 3.2. we have clearly shown that acetylene leads to atmosphericpressure deposition of nano-particulate solid layers of somewhat differing morphologies when the C₂H₂ "monomer" molecules with bond dissociation energy of 5.8 eV are subjected to suitable excitation energy. This occurs here in the PECVD case via Penning transfer from metastable Ar* ($E \sim 11.5 \text{ eV}$) or Ar₂* states in the DBD plasma; or, in the PICVD case, via photolysis, by absorbing 184.9 nm ($E \sim 6.70 \text{ eV}$) VUV photons. We estimate the respective power densities in the two reaction zones to be ca. 64 mW.cm⁻² and 58 mW.cm⁻², coincidentally close values; as shown in **Fig. 2**, we have also strived to keep the reactor geometries (along with operating parameters like pressure, 100 kPa, and 10 sccm C₂H₂ flow rate) constant. Both these processes appear to possess efficient gas-to-solid conversion efficiencies,^[19] albeit based on rather different reaction mechanisms. The lower PICVD deposition rate might be attributed in part to deposit buildup on the quartz glass that increasingly absorbs the lamp's emission. However, the impact of this phenomenon cannot be major, considering that the deposition time (10 min.) was less than the 20-30 min threshold where earlier experience in these laboratories

Under scrupulous exclusion of possible trace contaminants, especially oxygen, the solid "plasma- or VUV photopolymer" deposits are characterized by high-resolution (HR) XPS spectra that typify amorphous hydrocarbons, as seen in **Figure 5(a)** and **(b)**; curve fitting was done using state-of-the-art CasaXPS software. An important difference between the chemistry of the PECVD and PICVD coatings, which otherwise have rather similar characteristics and compositions, is highlighted in these spectra. But first, while XPS can not measure [H] content, we have very good reason to believe that the C/H ratio, = 1 in the C₂H₂ "monomer" molecule, is largely preserved in the solid deposits: Convincing and quite precise evidence for this comes from total combustion analysis (TCA) (using a Fisons Instruments, model EA1108 CHN elemental analyzer), and by Elastic Recoil Detection Analysis (ERDA) **[F]** of samples

represented in **Fig. 4(c)** [**E**]. The reader will also recall that even the earliest investigators had already concluded C/H ~1 [**C**, **D**]. The XPS C 1s peak fit of the PECVD films, **Fig. 5(a)**, shows that carbon in these coatings is predominantly in the sp³ hybridized state, while spectral analysis of the PICVD coatings, **Fig. 5(b)**, shows a majority of sp² carbon. Considering the nearly 1:1 C:H ratio, the chemistry of coatings obtained from more selective PICVD is expected to be closer to that of polyacetylene, while PECVD coatings, prepared in harsher plasma conditions, presumably contain less unsaturated bonds and more C-C crosslinks, and might therefore better be described as amorphous hydrogenated carbon, a-C:H.



Figure 5: High-resolution C1s XPS peaks from (a) PECVD; (b) PICVD under < 1 ppm O₂; (c) PICVD with small (but non-quantified) presence of O₂ contamination from residual air.

The presence of a tiny O₂ concentration during PICVD, regrettably not quantified in this work, but resulting from small air leak into the Plexiglass enclosure housing the (PECVD and

initial PICVD) reactors, greatly reduced deposition rate r on account of competing etch reactions. More important, however, is the fact that the initial solid PICVD deposit became exceedingly rich in oxygen, [O] ~ 55 at.% (Table 1) and highly soluble in water; Figure 5(c) is a corresponding HR XPS spectrum. Let us examine possible precedents for this.

Friedrich has long investigated the "big jump" in [O]/[C] ratios between O₂-plasma treated polyolefin surfaces, which can reach a maximum of roughly 28 at.%; evidently, the maximum possible O/C ratio of 2:1 is that of the CO₂ molecule.^[23,29] Water-soluble low molecular-weight oxidized molecules, so-called LMWOM,^[30] oligomer droplets created on polyolefins by excessive corona-discharge exposure, can have [O]/[C] up to 56%; they have been shown to include COOH, CHO, and CH₂-OH groups, as detected by gas chromatography.^[23,29] Inspecting the high-resolution HR XPS spectrum in **Figure 5(c)** leads one to believe that there may well exist much chemical and structural similarity between LMWOM, on one hand, and the photochemical reaction product from C₂H₂ PICVD with trace O₂ presence, on the other.

The foregoing text has exclusively dealt with study of a single hydrocarbon molecule, C₂H₂, so one may ask to what extent the PICVD / PECVD comparison presented here is "unique" to acetylene. Indeed, this is an opportunity to highlight the need to further explore photo-initiated systems: as PICVD appears to require more limited infrastructure than plasma, UV systems are interesting candidates to couple with other processes. However, PICVD has so far generally remained under-explored in the literature. In other words, there is interesting work to be conducted at the interface of two processes, if we can garner greater knowledge of PICVD. This work may be further motivated by the advent of UVC-emitting LED systems that forego the use of Hg and have found recent application in water treatment systems [31].

Recently, some of the present authors re-examined low-pressure PICVD of pure C₂H₂ feed gas, but this time at all four $\hat{\lambda}$ values in **Figure 1(a)**, thanks to the earlier-mentioned set of suitable commercial lamps.^[12] The authors found normalized deposition rate, r/Φ (where *r* is deposition rate, in nm s⁻¹, and Φ is photon flux, in ph cm⁻² s⁻¹) values of 2×10⁻¹⁸ (for $\hat{\lambda} = 147$

nm); 9×10^{-19} nm ph⁻¹ cm⁻² (at $\lambda = 124$ nm and $\lambda = 172$ nm); and 3×10^{-20} nm ph⁻¹ cm⁻² (at $\lambda = 185$ nm), roughly in line with *k* values in **Figure 1(a)**. They concluded as follows: "*It is noteworthy that pure acetylene-based, a-C:H films had been obtained in the past through PICVD by Danno and Hanabusa using a low-pressure Hg lamp. Their films were deposited at elevated temperatures (150 and 300°C), under conditions resulting in r/\Phi values of 1.8 \times 10^{-17} and 7.2 \times 10^{-18} nm ph⁻¹ cm⁻², respectively, compared to 3 \times 10^{-20} nm ph⁻¹ cm⁻² in the present work (at room temperature). Differences between setup geometries and process parameters (even though Danno also used p = 400 Pa = 3 Torr) could help explain the higher deposition rates obtained by the Japanese authors." Clearly, the photo-physical chemistry at atmospheric pressure (current work) cannot readily be compared with those results from low-pressure processes, where reactor geometries and fluid dynamics also play important complicating roles.*

The above-mentioned research has included work with both UVC (Hg lamp) and VUV [others, see **Figure 1(a)**] sources, using reagent gases other than C_2H_2 . In the former case, those have been syngas, a CO + H₂ mixture of variable ratio, with H₂O₂ as photo-initiator;^[32,33] reactions were carried out at reduced pressure, 20 kPa typically. However, quoting from Nasri *et al.*^[34], "*iron atoms appear in the coating, despite the fact that no iron was (intentionally)* added to the system. *GC–MS analysis reveals low concentrations of iron pentacarbonyl* [*Fe*(*CO*)*s*] are generated within the carbon monoxide cylinder. Its presence plays a determinant photocatalytic role in the reaction." Later, a heavier organic compound, methyl methacrylate (MMA) was successfully photo-polymerized at atmospheric pressure, albeit on the surface of a semiconducting photo-catalyst, TiO₂,^[35] as had already been reported by other workers.^[36] Even though MMA strongly absorbs UV below 275 nm, the polymerization rate is very low because of low decomposition and radical generation rates. Under UV irradiation TiO₂ promotes radical generation, thereby significantly boosting the MMA polymerization rate. In that research one was able to graft a PMMA-like film with a thickness of 1.5 nm on the surface of TiO₂ nanoparticles, confirmed by TEM, FTIR and XPS analyses.^[35] Since the objective of work by

Nasri *et al.*^[35] was to coat particles in a fluidized bed at ambient pressure and temperature with minimal additional infrastructure and associated costs, the UV PICVD approach was an attractive candidate, one that therefore deserves much further exploration. Clearly, the earlier-mentioned work by Zhang *et al.*^[11] on PMMA coating of NaCl nanoparticles at ambient pressure and temperature by irradiating MMA vapor with a Xe₂* excimer lamp at $\lambda = 172$ nm is closely related.

To summarize and conclude, we have here, for the first time, reported a comparison of two CVD processes carried out at atmospheric pressure using relatively low-cost apparatus, namely PECVD with a DBD plasma and PICVD with a low-pressure mercury vapor light source. Regrettably, there are few "simple" organic monomer molecules that permit such a study; here, we examined C_2H_2 . Under otherwise comparable experimental conditions, the following observations could be made:

- PECVD and PICVD both proved capable of converting C₂H₂ molecules into coatings of polymer-like solid material, albeit in the form of nano-particulate powder under the ambient temperature conditions exclusively studied here. The main differences between the PECVD and PICVD coatings were that the former mostly comprised sp³ carbon, while sp² was predominant in the latter; and that deposition rate was higher in the former case.
- Under the present working conditions PECVD was more "forgiving" than PICVD, because the latter called for virtually total absence of (even trace) contaminants, especially O₂;
- On the other hand, given a "clean" gas-handling infrastructure, it is arguable that lowpressure Hg UV light sources may be economically advantageous when compared with high-voltage DBD plasma reactors.

These questions certainly deserve closer examination in a subsequent extension of this research. Although there now exist efficient commercial VUV light sources, for example Xe excimer lamps,^[3] it is felt that these will remain restricted to highly specialized niche applications. On the other hand, there can be no doubt that PECVD with atmospheric pressure DBD or cold plasma-jet sources will continue to expand in a wide variety of industrial applications.

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CONFLICT OF INTEREST

The authors declare no financial or commercial conflict of interest.

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A pilot-scale reactor has been designed to operate in a dielectric barrier discharge (DBD) "PECVD" operating mode or in a photo-initiated "PICVD" one, the latter with low-pressure mercury lamps. Both processes operate at ambient temperature and atmospheric pressure, using acetylene (C_2H_2) monomer. Efficient gas-to-solid conversion can occur, in the form of nano-particulate amorphous hydrocarbon polymer-like deposits.