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Heterogeneous Growth of Continuous ZIF-8 Films on Low-Temperature Amorphous Silicon

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Abstract

Thin amorphous silicon films, deposited at low temperature by Inductively Coupled Plasma Chemical Vapor Deposition, have, for the first time, been employed as substrate for ZIF-8 growth. In order to investigate the role of the surface chemistry on the nucleation process, films have also been grown on other silicon-based substrates such as H-terminated Si(100), SiO₂ and quartz. Film preparation was carried out at room temperature using a mixed Zn nitrate and imidazole solution in methanol or ethanol. Using methanol, continuous ZIF-8 films were obtained on amorphous Si and H-terminated Si(100), while less homogeneous films were formed on the other surfaces. In ethanol, slower growth rates occurred and thinner films, compared to the ones in methanol, were obtained. These slower rates highlight the different effects of the four surfaces on the growth process. These differences have been related to the silanol density of the surfaces and to the Lewis basic strength which affect imidazole moiety deprotonation. H-terminated Si(100) and amorphous Si turned out to be the most reactive surfaces, whereas on quartz and, especially, on SiO₂ reactivity was much lower. Experimental results have been validated by the DFT modelling of the proton exchange, which takes place between the imidazole group and the surface. Finally, the VOCs adsorption capability of ZIF-8 films grown on amorphous silicon has been evaluated through temperature desorption experiments.

Keywords: *a-Si layer, ZIF-8 coating, surface chemistry, growth mechanisms, VOCs adsorption*

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Introduction

Metal Organic Frameworks (MOF) are becoming more and more promising for a wide range of technologies [1-6]. Similar to coordination polymers, MOF are hybrid porous complexes in which periodic arrangements of metal clusters are connected by organic ligands [7]. They have a flexible crystalline structure with tunable pore sizes, large surface area, chemical stability, and low density [8,9]. Zeolitic Imidazole Framework (ZIF) is a MOF category characterized by a sodalite-type structure with transition metal cations such as Zn, Co and Cd linked to imidazole ligands in a three-dimensional tetrahedral framework. Among all possible zeolite architectures, ZIF-8, i.e. $\text{Zn}(\text{MeIm})_2$ (HMeIm: 2-methylimidazole), presents a crystal bcc structure with lattice parameter of 16.32 Å, in which Zn^{2+} ions are coordinated to N imidazole atoms forming ZnN_4 clusters [10,11]. Its elastic framework is characterized by large openings of 11.6 Å accessible through six-membered ring apertures of 3.4 Å, which makes ZIF-8 structure suited for gas separation and adsorption [12,13]. Furthermore, for its high specific surface area ($\sim 1700 \text{ m}^2\text{g}^{-1}$), remarkable thermal resistance (above 550°C) and good chemical stability in water and organic solvents, ZIF-8 has also great potentialities for gas separation, chemical sensing, and energy devices [11,14-17]. Most of the synthetic methods used for ZIF-8 powders synthesis such as solvothermal, microwave-based, mechanochemical and sonochemical syntheses [18-21] are not suitable for film growth because they lead to cracks and defects [22,23]. It is also needed to overcome the poor heterogeneous growth of ZIF-8 and promote better adhesion and local crystallization. In this context, techniques like layer-by-layer deposition (LBL), liquid-phase epitaxy (LPE) and rapid thermal deposition (RTD) result more efficient in terms of thickness control and surface homogeneity [24-27]. The above-mentioned approaches have often been combined with surface modifications to optimize the chemical-physical compatibility between substrate and ZIF-8 precursors, thus suggesting the key role played by the nature of surface. Typical growth surfaces such as gold, glass and silicon can be functionalized with covalent binders, polymers [28-31], and, alternatively, with pre-deposited ZnO seed layers [31-33] to enable ZIF-8 nucleation and growth on the reactive centres.

In this context, the key factors determining ZIF-8 films nucleation and growth have yet to be understood to develop efficient synthetic approaches and obtain scalable and reproducible processes. Several studies on the other hand, focus not on layers but on the mechanisms involved in ZIF-8 particles homogeneous nucleation [34,35]. These studies suggest that the key step of ZIF-8 particle formation is the deprotonation of imidazole either as isolate molecule or as Zn-imidazole complex. For this reason, the polarity and/or basicity of solvents and of possible additives speed up the nucleation

and crystals growth [36,37]. However, the heterogeneous mechanisms and the parameters such as substrates and solvents nature determining film formation are still unclear, and, further work is required to understand film growth. The study of ZIF-8 growth on the amorphous Si (a-Si) surface is of particular importance because a-Si can be used to cover substrates not compatible with MOF growth and, therefore, considerably broadens the range of applications.

In this study, we focus on the role of two critical parameters (i.e. solvent and surface chemistry), during the growth of ZIF-8 films on Si-based substrates such as H-terminated Si, quartz, native SiO₂ and, in particular, a-Si, with the aim of developing efficient solution synthesis routes. Due to its cost-effectiveness and compatibility with several materials, a-Si is an highly promising system which makes easy the integration of a-Si grown ZIF-8 films into a large variety of devices. Continuous and homogeneous films capable of adsorbing aromatic and nitroaromatic VOCs have been obtained on both a-Si and H-terminated Si. Combining experimental chemical, structural, morphological and optical data with theoretical DFT modelling has afforded a more comprehensive view of the mechanisms involved in the heterogeneous growth process.

2. Experimental

2.1. Substrate preparation

Thin film substrate. Amorphous Si is a class of materials prepared using a number of techniques ranging from amorphization of crystalline Si by ion implantation to deposition from gas phase. [38,39] We deposited a-Si using an inductive-coupled plasma Chemical Vapour Deposition reactor which ensures a high plasma density ($\approx 10^{11}$ ions/cm³) and allows the deposition of a-Si at very low temperature, even on flexible and thermally sensitive materials. After high vacuum was established (5×10^{-7} Torr) in the process chamber, the a-Si was deposited at 50°C, 10 mTorr and 500 W using 20 sccm of pure SiH₄ gas and 1 sccm of Ar to ignite the plasma. An extensive structural characterization of low-temperature plasma grown layers had previously been performed elsewhere [40,41]. The H content measured by Elastic Recoil Detection Analysis (ERDA) is as high as 25% (Fig. S1 in the Supplementary Material) and the SiH peaks appear in the Raman spectrum in the 1900-2700 cm⁻¹ region [42]. Finally, layer thickness, measured by spectroscopic ellipsometry, was of 18 nm with a roughness of 1 nm.

Bulk substrates. Three different substrates have been used: native SiO₂ grown on Cz-Si(100) and quartz were used as received; H-terminated Cz-Si(100) was obtained by Cz-Si dipping in HF (1%) for

90s in order to remove the native SiO_2 . The substrate was then washed quickly in deionized water, dried under N_2 flow and immediately introduced in the reaction solution for ZIF-8 film growth.

2.2. ZIF-8 film growth

2-methylimidazole (HmeIm), $\text{Zn}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$, methanol (MeOH) and ethanol (EtOH) were purchased from Sigma-Aldrich and used as received. ZIF-8 films were grown through a one-pot method as reported by Lu et al. [43]. Briefly, two solutions of 250 ml of $\text{Zn}(\text{NO}_3)_2$ (12,5 mM) and 250 ml of HmeIm (25 mM) were prepared in MeOH and in EtOH. The substrates were then dipped in a mixture of 10 ml of $\text{Zn}(\text{NO}_3)_2$ and 10 ml of HmeIm solutions at room temperature for cycles of 30 min each without stirring. Subsequently the samples were rinsed in the reaction solvent (MeOH or EtOH) and finally dried under N_2 flow. Cycles ranging from one to ten were performed for both MeOH and EtOH solutions.

2.3. Sample characterization

Ellipsometric measurements were performed using a VASE instrument (J.A. Woollam) which is better suited for transparent samples in order to measure on the same position ellipsometric and transmittance data adopting a vertical 9-29 configuration. Optical spectra were recorded from 300 nm to 2100 nm at 55° , 60° and 65° incident angle values near the Brewster angle of the transparent substrate. The optical model was built for each layer constituting the sample. The layer thickness was initially evaluated by a simple Cauchy model assuming $k=0$ in the infrared spectral region. The complete ZIF-8 layer optical constant were modelled by using two gaussian oscillators. Special care was taken to evaluate the optical constants for the glass substrate taking into account backside reflection and un-polarized light. Data fitting has been obtained through the whole range of measurements (300–2100 nm) including transmittance data for better estimation of layer thickness.

XPS spectra were run with a PHI 5600 multi-technique ESCA-Auger spectrometer equipped with a monochromatic Al $K\alpha$ X-ray source. Analyses were carried out with a photo-electron angle of 45° (relative to the sample surface) with an acceptance angle of $\pm 7^\circ$. The XPS binding energy (BE) scale was calibrated by centering the C 1s peak due to hydrocarbon moieties and “adventitious” carbon at 285.0 eV. XPS atomic concentration was evaluated by estimating the integrated area of C1s, O1s, Si 2p, Zn 3p and N1s peaks corrected for the corresponding relative atomic sensitivity factor (S_x) based on empirical data reported by Wagner and corrected for the transmission function of the spectrometer.

Sensitivity factor for Zn 2p_{3/2} was empirically determined from ZIF-8 powders. Note that atomic concentration of Zn has been estimated averaging Zn 3p and Zn 2p₃ signals.

X-ray diffraction (XRD) patterns were collected with a D8 Discover (Bruker AXS) diffractometer equipped with a high-precision goniometer (0.0001°), a thin-film attachment (long sller slits) and a Cu-K α source. The acquisitions were done in grazing incidence geometry with incident angle of 0.4°. This corresponds to a penetration depth of approximately 50 nm. The acquisition time was the same for all the diffraction patterns.

Field emission scanning electron microscope (Zeiss Supra35 FE-SEM) equipped with EDX microanalysis system (Oxford Instruments, X-MAX, 80 mm²) was used to observe morphology. Gas adsorption was evaluated by exposing samples to vapors of aromatic compounds according to previously reported approaches [44, 45]. Briefly, vapor adsorption was obtained by placing a-Si grown ZIF-8 films for 30 min in a closed chamber saturated at 25°C with toluene, nitrobenzene and water vapors (vapor pressures of about 3x10³ Pa, 30 Pa and 3x10³ Pa, respectively, calculated according to the Antoine equation [46]). For thermal desorption experiments, ZIF-8 films were resistively heated (4 °C/min) in a UHV chamber (basic pressure ~ 10⁻⁸ Torr) from 25 °C to 210 °C and desorbed molecules were detected with a Smart-IQ+ (Thermo Electron Corporation) quadrupole mass spectrometer equipped with an electron filament as ion source.

2.4. Computational details

DFT-based simulations were performed with the CP2K/Quickstep package, using a hybrid Gaussian and plane wave method [47]. A double quality DZVP Gaussian basis set was employed for all atoms. The Goedecker-Teter-Hutter [48] pseudopotentials together with a 400 Ry plane wave cutoff were used to expand the densities obtained with the Perdew-Burke-Ernzerhof (PBE) [49] exchange-correlation density functional. A surface dipole correction was employed along the z axis to avoid unrealistic dipole interactions among the slabs [50]. Molecular graphics were produced by the CHEMCRAFT graphical package [51]. Solvent effects were taken into account for the proton release process of the imidazole molecule by using the self-consistent continuum solvation (SCCS) model of Andreussi et al. [52]. The Zn²⁺ coordinated imidazole was modelled using two methyl groups and two imidazole groups with a tetrahedral environment around the Zn center. In order to model surface structures, bulk Si and quartz cell were optimized. On the optimized bulk cells, the 100 plane was cut for both Si and SiO₂. A seven-layer slab was built using a 20 Å vacuum region between slabs. The coordinates of the deepest layer were fixed to model bulk constrains.

3. Results and discussion

3.1. Growth rate and optical properties of ZIF-8 films grown from MeOH and EtOH solutions

ZIF-8 films have been grown on transparent substrates (i.e. glass or quartz) adopting MeOH and EtOH to evaluate the effects of the solvent on the film growth process. Films were first characterized by spectroscopic ellipsometry in order to obtain information on the thickness, growth rate, and on the optical properties such as the refractive index and the extinction coefficient which, to the best of our knowledge, were not yet reported for ZIF-8 layers.

Fig.1 ZIF-8 growth rate and refractive index as measured by Spectroscopic Ellipsometry as a function of the solvent (MeOH or EtOH) and process methodologies (multi- or single-step)

Fig. 1 shows how solvents affect the growth of films prepared using various deposition cycles of 30 min each (multi-step process). The MeOH solvent determines a faster growth rate compared to EtOH

for all the investigated dipping times. In addition, the growth rate duration of each cycle strongly influences the overall film thickness because it decreases after a 30 min single dip. This behavior indicates that a 30 min multi-step process is optimal to prepare thick ZIF-8 films because a long single process does not guarantee a constant growth rate. The refractive index, measured with the Cauchy formula between 1 and 2 eV, where the layer is transparent ($k = 0$), increases and tends to saturate above 200 min in both solvents but it is higher in MeOH attesting that films grown from MeOH are denser than the ones grown from EtOH.

Fig.2 Refractive index and extinction coefficient of ZIF-8 as measured by Spectroscopic Ellipsometry in layers of similar thickness (60nm) prepared with different solvent.

Fig. 2 shows that the refractive indexes of samples obtained using MeOH and EtOH have a similar dependence on the photon energy. These values are low compared to other materials attesting the typical “empty” structure of the framework. Nevertheless, ZIF-8 layer prepared in MeOH has a higher refractive index (see also Fig. 1) over the whole investigated range (from infrared to the deep UV) compared to layer prepared in EtOH. This can be attributed to the formation of a denser layer, being on purpose the thickness of 60 nm in both cases. Furthermore, both layers have the same edge of the

extinction coefficient which evidently attest a similar band gap, which is typical of material itself and does not depend on the preparation method.

3.2. Role of the substrate surface on ZIF-8 growth

ZIF-8 films have been grown on a-Si and other three Si-based substrates (SiO_2 , quartz, and Si) to investigate the role of the surface chemistry on the deposition process.

Low and high-magnification SEM images of film obtained after 10 deposition cycles are reported in Fig. 3.

Fig. 3 SEM images of ZIF-8 layers grown through 10 deposition cycles on Si (a,d), a-Si (b,e) and quartz (c,f) from MeOH (a-c) and EtOH (d-f).

Film growth in MeOH on Si and a-Si leads to continuous coatings, which consist of homogeneous well-formed crystals (Fig. 3 a and b). A less homogeneous film with large crystals embedded in a layer of tiny grains was obtained on quartz substrate (Fig. 3c). For this substrate, several cracks are also visible in the SEM micrographs. Using EtOH as solvent, less continuous coatings, in some cases with large uncovered areas, have been obtained (Fig. 3d-f). The substrate coverage is higher on Si, and it decreases moving from Si to a-Si and to quartz. On SiO₂ SEM analyses is not shown because, in both solvents ZIF8 growth is negligible. EDX analyses performed on all samples (Fig. S2 and Table S1 in the Supplementary Material) confirmed the presence of all ZIF-8 elements. In addition, the trend of ratios (R) between Zn and the substrate (Si+O) atoms ($R = \text{Zn}/(\text{Si}+\text{O}) \times 100$) confirmed that thicker coverages can be obtained from methanol on Si, a-Si and quartz ($R = 1.3, 1.3$ and 1 , respectively) compared to film grown from ethanol ($R = 0.3, 0.3$ and 0.1 for Si, a-Si and quartz). A negligible ZIF-8 growth resulted on SiO₂ from both methanol and ethanol ($R \sim 0.1-0$).

Further indications on the role of the surface on the film growth have been obtained through the XPS characterization. Table 1 reports the chemical compositions of ZIF-8 films obtained from XPS analyses. The atomic concentration obtained from a ZIF-8 powder has been added as reference.

The films grown on Si and a-Si show a composition similar to that of bulk ZIF-8 powders. The C/N/Zn atomic ratio for films and reference is about 15/4/1 in which the N/Zn ratio is equal to the theoretical value (4/1). The carbon excess compared to the nominal values (C/Zn nominal = 8/1) is due to the ubiquitous presence of “adventitious” C. In This result is consistent with the presence of a well-formed and continuous coverage of ZIF-8 crystals.

The N/Zn atomic ratio slightly changes moving from Si and a-Si, to quartz and SiO₂, decreasing from 4.2 and 4.1 to 3.5 and 2.7, respectively. This decrement is more evident for samples grown from EtOH on quartz and SiO₂. N/Zn ratios lower than those expected for well-formed ZIF-8 layers are measured for samples with lower coverages (see Table 1 and Fig. 3), because of the lower growth rate.

The N 1s and Zn 2p_{3/2} XPS peaks of all samples are centred in the same regions observed for ZIF-8 powder, at 399.3 eV and 1023.1 eV respectively, thus suggesting the formation of Zn-N coordination bonds typical of ZIF-8 crystals.

<i>XPS Atomic Concentration %</i>						
<i>Reaction solvent MeOH</i>						
SAMPLE	Si	C	O	N	Zn	N:Zn
Si	0.9	71.4	3.9	19.2	4.6	4.2
a-Si	0.1	71.8	3.0	20.2	4.9	4.1
Quartz	0.9	67.8	5.9	19.8	5.7	3.5
SiO ₂	37.7	18.7	36.1	5.3	2.1	2.7
<i>Reaction solvent EtOH</i>						
	Si 2p	C 1s	O 1s	N 1s	Zn	N:Zn
Si	1.4	73.2	7.2	14.6	3.6	4.0
a-Si	11.5	52.2	16.6	15.6	3.9	4.0
Quartz	21.8	22.8	46.4	5.8	3.3	1.75
SiO ₂	39.0	24.1	34.8	1.4	0.8	1.75
<i>Reference</i>						
powder		67.2	2.5	24.4	5.9	4.1

Table 1: XPS atomic concentration of ZIF8 films grown on the four substrates from MeOH and EtOH solutions. The XPS atomic concentration of ZIF-8 powders has been added as reference

Fig. 4 left shows XRD patterns of ZIF-8 films grown from MeOH solutions through 10 deposition cycles of 30 min each. Patterns of samples grown on a-Si and Si consist both of a main diffraction peak at $2\theta = 7.4^\circ$ arising from (011) planes of a crystalline ZIF-8 structure, which, according to both the data from Crystallographic Open Database (COD) [53,54] and previous literature [24,55], is the most intense ZIF-8 peak. The other reflections are hardly detectable from the background noise due to the low amount of deposited materials. Only the low intense reflections at $2\theta = 10.3^\circ$, 12.8° and 14.8° (002, 112 and 022, respectively) can be detected in the pattern. In addition, note that the higher intensity of 011 and 022 reflections compared with the simulated pattern suggests the presence of a preferential orientation along the [011] direction [24].

Fig. 4 XRD diffraction pattern of ZIF-8 grown through 10 deposition cycles on Si and a-Si surfaces from MeOH (left) and EtOH (right). The simulated pattern from reference data [53,54] was also added.

The full width at half maximum (FWHM) accounts for ordered crystallites of average size 35 nm for Si as estimated using the Scherrer formula ($D = 0.9\lambda/\beta\cos\theta$, being β a function of the FWHM, corrected with the instrumental broadening). The interplanar spacing for the (011) planes is 1.19 nm. A slightly different scenario can be depicted on a-Si: the peak is less intense, the d-spacing is 1.2 nm and the average crystallites size is 40 nm. It has to be noted that the same ZIF-8 materials using EtOH as solvent have been obtained, although due to the lower growth rates less intense peaks are observed (Fig. 4 right).

3.3. ZIF-8 Heterogeneous mechanisms: experimental and theoretical modeling

In order to make evident the substrate role during the initial stages of film growth and to investigate the initiation of ZIF-8 deposition, short-time deposition processes (10 min), have been carried out on the four surfaces using MeOH and EtOH. The obtained samples have been characterized by XPS spectroscopy.

Fig.5 XPS spectra of N1s (a) and Zn 2p_{3/2} (b) regions of ZIF-8 films grown on the four substrates from MeOH (left) and from EtOH (right)

Fig. 5 shows the N 1s (a) and Zn 2p_{3/2} (b) bands of ZIF-8 samples grown on the four substrates. For all samples, N 1s signals consist of two components, at 399.3 (N_a) and 400.8 eV (N_b). The BE value of the lower energy components of N 1s is similar to the value observed for bulk ZIF-8 and it is due to deprotonated imidazole nitrogen atoms. The N_b component is likely due to not-deprotonated N-H moieties of unreacted adsorbed imidazole molecules. The relative intensity of the two components varies as function of the solvent and substrate (Table 2). In MeOH, samples grown on Si, α-Si and quartz mainly show the N_a component which is associated to fully formed ZIF-8. On the other hand, on SiO₂ the intensity of the two components is similar, thus indicating that the nucleation on SiO₂ is much slower than the one observed on the other 3 surfaces. In EtOH, the intensity of the 400.8 eV component related to not-deprotonated imidazole is higher than those of the corresponding samples in MeOH and,

in particular, the N_a/N_b ratio decreases with the following order: Si>a-Si>>quartz>SiO₂. The above reported results indicate that i) nucleation in EtOH is slower compared that in MeOH, and ii) heterogeneous nucleation rate increases with the following order SiO₂<quartz<<a-Si< Si.

Zn 2p_{3/2} band can be also described as sum of two components, at 1023.1 (Zn_a) and 1024.2 eV (Zn_b). The BE of the first component is similar to that observed in bulk ZIF-8. The second component can be associated to hydroxides or nitrates.

	MeOH			EtOH		
	N/Zn	N _a /N _b	Zn _a /Zn _b	N/Zn	N _a /N _b	Zn _a /Zn _b
Si	4.3	15.9	8	2.1	4.8	8
a-Si	3.7	14.6	7	1.5	3.1	9
Quartz	2.7	7.4	5	2.9	1.0	2
SiO ₂	3.1	1.4	5	1.3	0.9	2

Table 2: XPS atomic and main component ratios of N and Zn of ZIF8 films grown on the four substrates from MeOH and EtOH.

Similarly to N 1s band, the different intensity ratios of these two components as function of the substrate and solvent can be associated to different nucleation rates. Data on Zn components confirm the results observed for N 1s signal, although differences between a-Si and Si are less evident, because the Zn_a/Zn_b ratio increases following the trend EtOH<MeOH and SiO₂≤quartz<<a-Si≤ Si.

DFT calculations have been performed to rationalize the above reported effects of solvents and surfaces on the starting steps of the ZIF-8 deposition. Previous literature studies [34,56] on the homogeneous formation of ZIF-8 indicated that the key step for the crystal growth is the imidazole deprotonation either of isolate imidazoles [34] or of Zn²⁺ coordinated imidazoles [56]. Hence, the deprotonation energies of the imidazole and the Zn²⁺ coordinated imidazole have been compared. It was found that the process is favored for the Zn complex of about 15 kcal/mol compared to the imidazole. Moreover, when the process is modelled in MeOH or in EtOH similar stabilization effects were observed. In particular, methanol induces slightly better stabilization than ethanol ($\Delta = 0.5$ kcal/mol) due to the slight different dielectric constants ($\epsilon = 24.852$ D for ethanol and $\epsilon = 32.613$ D for methanol).

Fig. 6 The modelled starting deposition step used in DFT calculations to compare the different surfaces

Figure 6 shows the proton exchange between the Zn complex and the hydroxyl groups on the surface, followed by the formation and displacement of water along with the coordination of the complex onto the surface (Fig. 6). This initial step leading to the formation of an adsorbed intermediate is endergonic, and it can be seen as an energy barrier for the subsequent steps of the ZIF-8 growth. Since deprotonated imidazole must interact with Zn^{2+} ions to form ZIF-8 crystals [34, 56], it is reasonable to assume that also the deprotonated adsorbed intermediate reacting with adsorbed Zn^{2+} yields the ZIF-8 film (Fig. 6).

In order to compare the four surfaces we modelled this initial deprotonation step adopting, instead of the Zn complex, the simpler imidazole. We modelled four Si(100) surfaces characterized by a different oxygen content: a) with one hydroxyl group, b) with two oxygen groups, c) saturated of hydroxyl groups and, d) a totally hydroxylated $\text{SiO}_2(100)$ surface (see Fig. 7).

Fig. 7 Surfaces adopted to simulate the first step of the ZIF-8 growth: a) Si(100) with one hydroxyl group; b) Si(100) with two vicinal hydroxyl groups, c) Si(100) saturated of hydroxyl groups, d) totally hydroxylated SiO₂(100)

It was found that the preferred surface on which the first ZIF-8 deposition process occurs is the Si(100) with one hydroxyl group (Fig. 7a). Using surfaces with higher oxygen content the process is more energy demanding. In particular, on Si(100) with two hydroxyl groups (Fig. 7b), the process requires 2 kcal/mol extra, on Si(100) saturated of hydroxyl groups (Fig. 7c) 2.7 kcal/mol extra and on the SiO₂(100) surface (Fig. 7d), 13.1 kcal/mol extra. It appears clear that higher the oxygen content and, in turn, the hydroxyl density, on the surfaces, higher the inhibition of the ZIF-8 deposition on the surface in good agreement with experimental data.

Si and a-Si surfaces which mainly consist of hydride (Si-H_x) terminations with a low density of hydroxyl groups (Si-OH silanols) due to oxidation phenomena, represent the most reactive substrates because of isolated silanols are free to react and to promote proton exchange. The reactivity of hydroxyl groups decreases by increasing their density due likely to a cross linking of H-bonds and by increasing the overall oxygen content, thus making quartz a less reactive surface compared Si. Native SiO₂ resulted the less reactive surface because of the high density of silanols which form rigid siloxane bridges that prevent direct functionalization.

More experiments were performed in order to explore the role of Zn²⁺ ions on the ZIF-8 formation following the imidazole moiety deprotonation (Fig. 6). In these experiments, each surface was treated (10 min) with a Zn(NO₃)₂ ethanol solution, rinsed in ethanol, dried under N₂ flow and then analyzed by

XPS to evaluate surface Zn^{2+} adsorption. For all 4 surfaces, spectra show the presence of Zn 2p_{3/2} band at 1024.2 eV attributable to adsorbed Zn^{2+} species, such as hydroxides or nitrates (Fig. S3 in the Supplementary Material). However, the amount of adsorbed ions, evaluated through the atomic ratio between Zn and the substrate atoms (i.e Si and O) (Table 3), is much lower for SiO_2 compared to the other three surfaces. The low amount of adsorbed Zn^{2+} ions available to interact with the adsorbed intermediate, combined (see above) with the calculated high energy barrier (13.1 kcal/mol), accounts for the negligible ZIF-8 growth observed on SiO_2 surfaces.

Substrate	Si	C	O	Zn	$\frac{\text{Zn}}{(\text{Si} + \text{O})} \times 100$
Si	41.9	35.9	21.4	0.8	1.3
a-Si	25.8	37.5	35.7	1	1.6
Quartz	30.9	13.2	54.9	1	1.2
SiO_2	37.7	28.2	34.0	0.1	0.1

Table 3. Atomic concentrations of the four surfaces after treatment (10 min) with $\text{Zn}(\text{NO}_3)_2$ ethanol solutions (12.5 mM)

3.4 Aromatic VOCs adsorption/desorption

The gas adsorption capabilities of ZIF-8 film grown on a-Si layers have been tested through a set of adsorption / desorption experiments. In particular, ZIF-8/a-Si bilayers have been exposed for 30 min to a mixture of toluene, nitrobenzene and water (100:1:100) vapors and, then, the desorption of adsorbed gasses upon heating was studied by in situ mass spectrometry.

Fig. 8. Thermal desorption experiment of ZIF-8/a-Si bilayers after adsorption of a toluene/nitrobenzene (100:1) mixture.

During thermal desorption, the main ions observed are $C_7H_8^+$ and $C_7H_7^+$ (Fig. 8) which arise from toluene fragmentation, but also $C_6H_5^+$ and $C_6H_5NO_2^+$ ions, which are typically found in the nitrobenzene mass spectra, have been detected. No significant water desorption was observed during the heating. This findings indicate that both aromatic and nitroaromatic VOCs can be adsorbed on the a-Si grown ZIF-8 films even in the presence of water-rich environments and, therefore, these films maintain the typical adsorption properties of bulk ZIF-8 powders.

4. Conclusions

Combination of experimental and theoretical results has given a coherent explanation of the effect of surfaces and solvents on the heterogeneous growth of ZIF-8 films. Growth process has been model through the proton exchange between the imidazole moiety either as free molecules or, more likely, as Zn-imidazole complex and the surface silanols groups. Both experimental and theoretical results indicate that this process is stabilized by polar solvent such as MeOH which induces a better stabilization compared EtOH. As regard the surface role, results indicate that the oxygen content on the surfaces and, also, the silanols densities affect the proton exchange process and the imidazole deprotonation. For these reason, H-terminated Si and low-temperature (50°C) CVD grown amorphous silicon resulted more suited to ZIF-8 film growth compared to both oxygen rich quartz and SiO_2 surfaces.

Finally, the capability of a-Si grown ZIF-8 films of adsorbing aromatic and nitroaromatic vapors has been demonstrated through temperature desorption experiments.

The above-mentioned outcomes are of particular importance to better understand the heterogeneous growth of ZIF-8 films. This aspect of ZIF-8 is of great relevance because many of its potential applications such as gas separator membranes, sensing layers and energy storage devices require its use as thin film. Furthermore, the ZIF-8/a-Si system represents a novel multi-layer structure that allows a wider range of MOF applications. Indeed, by modulating the morphology and the chemical-physical properties of a-Si and of ZIF-8, it is possible to design new integrated materials for specific applications.

Declaration of interests: none.

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Supplementary Material

Supplementary data to this article can be found on line.

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Highlights

- ZIF-8 films were grown for the first time on CVD deposited amorphous Si layers
- The role of solvents and surface chemistry on the growth process was studied
- The silanol density and the Lewis basic strength of the surfaces affect the relevant reaction steps
- Experimental results were validated by the DFT modelling of the proton exchange

Graphical Abstract