



Full Length Article

Nucleation and growth of microdroplets of ionic liquids deposited by physical vapor method onto different surfaces



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ABSTRACT

Nanoscience and technology has generated an important area of research in the field of properties and functionality of ionic liquids (ILs) based materials and their thin films. This work explores the deposition process of ILs droplets as precursors for the fabrication of thin films, by means of physical vapor deposition (PVD). It was found that the deposition (by PVD on glass, indium tin oxide, graphene/nickel and gold-coated quartz crystal surfaces) of imidazolium [C₄mim][NTf₂] and pyrrolidinium [C₄C₁Pyrr][NTf₂] based ILs generates micro/nanodroplets with a shape, size distribution and surface coverage that could be controlled by the evaporation flow rate and deposition time. No indication of the formation of a wetting-layer prior to the island growth was found. Based on the time-dependent morphological analysis of the micro/nanodroplets, a simple model for the description of the nucleation process and growth of ILs droplets is presented. The proposed model is based on three main steps: minimum free area to promote nucleation; first order coalescence; second order coalescence.

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1. Introduction

Ionic liquids (ILs) are an important field of research of the past years, converging on the ultimate purpose of large scale industrial applications [1–3]. They are made of a cation and an anion held together by a wide range of intermolecular forces from weak and isotropic to strong and highly directional ones. ILs are commonly defined as organic or inorganic salts with melting temperatures below 373 K. Due to the several combinations of ion pairs, there are innumerable ionic liquids with different physical and chemical behaviors which have been deeply studied by different research groups [4–8]. Generally, ILs share mutual features, such as the ionic conductivity, high thermal stability and viscosity and low vapor pressure at room temperature [9,10].

Nowadays, the model that explains ionic liquids bulk properties is based on the formation of a network made of polar and nonpolar domains giving rise to a nanostructured molecular arrangement

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[11]. Nevertheless, this behavior is a trend that these liquids follow with the increasing of the alkyl chains which after a specific number of carbons segregate into solvophobic regions [11,12]. Although the bulk properties of ILs have been advantageously utilized in many fields ranging from, green energy and environment [13] to cellulose processing [14], their interfacial behaviour is considered as very promising in energy storage [15], electrochemistry [16], crude oil industry [17], pesticides industry [18], and particle self-assembly [19], among others. This emerging subject focuses on the research of the surface layer and the near surface structure when in presence of a solid, liquid or gaseous interface. Considering the nanostructuring referred before it is expected that the addition of a macroscopic interface leads to the formation of a different, but related, molecular arrangement. Molecular level approaches to this behavior have been made mainly through computational methods namely Pensado by et al. who studied, using molecular simulations, the effect of the length of imidazolium cation's alkyl side chain and the presence of an end hydroxyl group at its end at IL/vapor interface concluding that the alcohol groups led to a lowering of the organization of the liquid phase [20] and Kirchner et al. who observed at charged surfaces a multilayered to a monolayered transition of the electrical double layer using a coarse grained model [21]. Experimentally, the surface tension, contact angles and wettability of ILs in polar and nonpolar polar substrates has been

measured, however, only general trends have been identified so far [15,22,23]. Independently of the polarity of the substrates, ionic liquids with maximum and minimum surface tension had higher and lower contact angles, respectively, and their anions play a relevant role on their wettability on the contrary of the alkyl side chain length and cations which seem to have a smaller impact. Furthermore, X-ray photoelectron spectroscopy (XPS) has given insights about ILs structure when at the interface with vacuum showing an enrichment of the alkyl side chains outwards the bulk [24,25].

Moreover, due the negligible vapor-pressure of ionic liquids, a new field of study dedicated to thin films of ionic liquids and their application in nano-surface science and technology has been generated. Gusain et al. have shown the great potential of ILs to reduce the friction in micro/nano electromechanical systems by preparing an IL thin film on a silicon substrate with a self-assembly approach via covalent linkage [26]; Wang and Priest studied the wetting behavior of a family of imidazolium ILs as precursor thin films in mica using atomic force microscopy (AFM) having concluded that the presence of an agent that covers the surface completely or partially prevents the growth of the IL film and slows the contact angle relaxation [27]; Maruyama et al. have developed a new method for the synthesis of “nano-IL” through molecular beam deposition of the IL in ultrahigh vacuum [28]; finally, Cremer et al. reported the preparation and XPS characterization of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)-imide [C₂mim][NTf₂] thin film on a glass substrate using an *in situ* thermal-evaporation/condensation process under ultrahigh vacuum conditions [29].

Our work aims for the production of micro/nanodroplets as precursor thin films of ionic liquids, by mean of physical vapor deposition (PVD), and its morphological study by scanning electron microscopy (SEM). In a previous work, the morphology of droplets and thin films of a series of imidazolium based ILs prepared through PVD on indium-tin-oxide-coated glass (ITO) was presented and the results showed the nanostructuring of ionic liquids [30]. In this study we have performed the vapor deposition of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)-imide [C₄mim][NTf₂] and 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide [C₄C₁Pyrr][NTf₂] on chemically different substrates – glass, ITO, graphene and gold. A model for the nucleation and growth mechanism of micro/nanostructures of these materials is proposed.

The formation of thin films is highly regulated by kinetic as any complex transport property, involving phase transitions, interface potentials, molecular diffusion at the surface leading to a complex landscape of metastable local minimums of potential that in the limit of uniform film reaches the thermodynamic equilibrium. Nucleation processes involves the creation of a high are/volume proportion implying the existence of a critical nucleus radius, the minimum size that must be formed by atoms or molecules clustering. The Gibbs energy associated to the formation of a solid and spherical nucleus can be derived by Eq. (1) [31,32].

$$\Delta G = a_3 r^3 \Delta G_V + a_1 r^2 \gamma_{l-v} + a_2 r^2 \gamma_{l-s} - a_2 r^2 \gamma_{s-v} \quad (1)$$

The magnitude of ΔG is dependent of the volume free energy associated to the condensation of vapor, ΔG_V , of the interfacial tensions (γ) of the triphasic system created at the surface (l is the liquid, v is the vacuum and s is the solid) and of the geometric components of the nucleus formed ($a_1 r^2$ is the area of the curved surface, $a_2 r^2$ is the circular area projected on the substrate and $a_3 r^3$ is the nucleus volume). The critical nucleus radius (r_{cr}) can be calculated by Eq. (2), considering the thermodynamic equilibrium: $d(\Delta G/dr)=0$.

$$r_{cr} = \frac{-2(a_1 \gamma_{l-v} + a_2 \gamma_{l-s} - a_2 \gamma_{s-v})}{3a_3 r \Delta G_V} \quad (2)$$

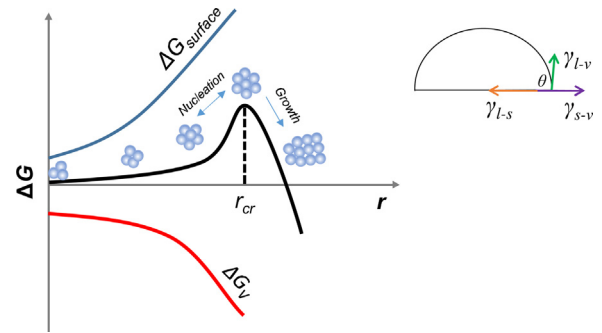


Fig. 1. Schematic representation of the change in Gibbs energy of a system for the process of nucleation and growth of thin films.

The Gibbs energy of a system when $r=r_{cr}$ (ΔG_{cr}) is given by Eq. (3).

$$\Delta G_{cr} = \frac{4(a_1 \gamma_{l-v} + a_2 \gamma_{l-s} - a_2 \gamma_{s-v})^3}{27a_3^2 \Delta G_V^3} \quad (3)$$

The thermodynamic state of the nucleation process, associated with the formation of stable nucleus with a minimum radius (r_{cr}), is reached when the volumic component is higher than surface energy, as schematized by Fig. 1.

The nucleation and growth of thin films can be described by three distinct models: Frank-van der Merwe growth (FM/2D growth); Volmer-Weber growth (VW/3D growth); Stranski-Krastanov growth (SK growth). The 2D growth (layer by layer) is favored when $a_2 r^2 \gamma_{s-v} \geq a_1 r^2 \gamma_{l-v} + a_2 r^2 \gamma_{l-s}$. This layer-by-layer growth indicates that complete films form prior to growth of subsequent layers. In opposition, the 3D growth (island formation) is favored when $a_2 r^2 \gamma_{s-v} < a_1 r^2 \gamma_{l-v} + a_2 r^2 \gamma_{l-s}$ whereby thin films grow epitaxially at a solid surface or interface. The SK growth is a combination of 2D and 3D growth mechanisms [31,32].

2. Experimental section

2.1. Reagents

The ionic liquids used in this work, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)-imide [C₄mim][NTf₂] and 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide [C₄C₁Pyrr][NTf₂], were purchased from IOLITEC with a state purity of >99%. Before each vapor deposition, the ILs were dried under low pressure (<10 Pa) and stirred continually for a minimum of 48 h at 373 K to reduce the presence of water and volatile contents. Before the deposition experiments, the low content of water (<500 ppm) was measured and confirmed by Karl-Fischer. Additionally, the water content was highly reduced inside the vacuum chamber.

2.2. Substrates

ILs micro/nanostructures were prepared on the surface of chemically different substrates: glass, indium tin oxide (ITO), graphene/nickel (G/Ni) and gold-coated quartz crystal. All surfaces were carefully cleaned first with acetone followed by isopropyl alcohol in an ultrasonic bath and dried with nitrogen. Surfaces and samples were stored in vacuum to avoid contamination.

2.3. Physical vapor deposition (PVD)

The PVD methods describe a diversity of vacuum deposition techniques that are usually more environmental friendly than traditional coating methods in solution. Droplets of ionic liquids were

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