Substrate effects in chemical solution deposition.

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One of the often-stated advantages of chemical solution deposition (or chemical bath deposition – abbreviated here to CBD) is that substrates of many different natures and essentially any shape can be coated uniformly. The latter is a consequence of the fact that most CBD processes are not diffusion controlled. However, the nature of the substrate may still be important. In principle, most clean surfaces can be used as substrates, although the degree of adhesion can vary greatly from one material to another. Even Teflon has been used as a substrate in a number of depositions, which shows the ability of CBD to form films on a wide range of substrates.

In common with other deposition techniques, rough surfaces (rough on the microscale) tend to give more adherent films than corresponding smooth ones. This is probably due to the greater actual surface area of contact per geometric surface area and the possibility of anchoring of the initial deposit in pores of the substrate.

Glass is one of the most commonly-used substrates in CBD. In spite of the fact that glass is a relatively inert material, the *surface* of glass can be very reactive towards species in solution. The surface of glass (and other oxides such as SnO_2-coated glass) is hydroxylated in aqueous solution and the surface hydroxide groups can form fairly strong hydrogen bonds.

$$\text{--Si-OH}^- \rightleftharpoons \text{--Si-O}^- + H^+$$

The concentration of the various species at the surface is therefore pH dependent, and this should be taken into account when choosing a suitable pH for the deposition solution (particularly for deposition from acid solutions). In addition, there are many different types of glass and some make better substrates (in terms of film adhesion) than others. In particular, glasses which contain a high concentration of heavy metal oxides are generally better in this respect than, for example, pure quartz or glasses with little heavy metal content, as was already shown a long time ago.[1] This was ascribed to the ability of the heavy metal atoms at the glass surface to bind chemically to constituents (e.g., S-containing species) of the solution. The possibility of ion exchange between metal ions in the glass and those in solution may also play a role in binding the initial CD film.

Glass substrates can be sensitized, usually with a solution of $SnCl_2$, which hydrolyses to give nuclei of tin hydroxide or oxide, on the surface. While in most cases of CD, such sensitization is not used, and not required, there have been many reports of better layers (more adherent and/or homogeneous layers, faster deposition) using such sensitization. Additionally, film formation on sensitized glass sometimes occurs (at least initially) in the absence of bulk precipitation in solution in contrast to the parallel film deposition and bulk precipitation which occurs when non-sensitized glass is used.[2] This suggests that a high supersaturation is required for nucleation to occur on untreated glass (as well in solution) and that this is not the case when nucleii are already present on the glass from the sensitization.

Metals make good substrates in general, either because chalcogenides tend to adsorb strongly on many metals, or the non-noble metals are covered with a (hydroxylated in the deposition solution) oxide layer. If the metal in the deposition solution has a sufficiently negative potential, an internal electrochemical reduction may occur.[3]

A large variety of CBD films have been deposited on different polymer surfaces. While deposition sometimes is satisfactory on the clean polymer, various activation treatments, such as treatment with permanganate, have been used to improve the adhesion and homogeneity.[4]

Films have also been deposited on monolayers. Hydrophilic and specific end groups on the monolayer molecules can bind species from the solution by chemical (e.g., a thiol end group will bind most metal ions) or electrostatic interactions. Since deposition (from aqueous solution) will normally not occur on hydrophobic end groups, patterning of CBD films on monolayers has been accomplished by patterning the monolayer end groups, often by light-induced changes in the chemistry of the monolayer.[5,6]

Apart from adhesion, the crystallographic properties of the CD film are sometimes dependent on the nature of the substrate One example is epitaxial deposition on a crystallographically-ordered substrate.[7-9] Also, even if the deposition is not epitaxial different texturing of the film may occur. A monolayer-covered substrate may also dictate the crystallographic form of a CD film depending on the interaction between the monolayer endgroups and the semiconductor.[10] Epitaxy strongly implies that deposition occurs by an ion-by-ion mechanism rather than by a cluster growth. For a cluster growth to give epitaxial films, the individual crystals in a cluster would at some stage have to align themselves with the substrate lattice. An ion-by-ion growth is much more likely to be directed by the substrate.

References

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