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Fabrication of complex oxide microstructures by combinatorial chemical beam vapour deposition through stencil masks

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ABSTRACT

Chemical Beam Vapour Deposition is a gas phase deposition technique, operated under high vacuum conditions, in which evaporated chemical precursors are thermally decomposed on heated substrates to form a film. In the particular equipment used in this work, different chemical beams effuse from a plurality of punctual precursor sources with line of sight trajectory to the substrate. A shadow mask is used to produce 3D-structures in a single step, replicating the apertures of a stencil as deposits on the substrate. The small gap introduced between substrate and mask induces a temperature difference between both surfaces and is used to deposit selectively solely on the substrate without modifying the mask, taking advantage of the deposition rate dependency on temperature. This small gap also enables the deposition of complex patterned structures resulting from the superposition of many patterns obtained using several precursor beams from different directions through a single mask aperture. A suitable process parameter window for precursor flow and substrate temperature is evidenced to maximize resolution.

1. Introduction

There is a growing demand for micro and nanofabrication technologies, to enable device miniaturization and integrated multifunctionality [1,2]. In particular, complex oxides, with their multifunctional properties offer tremendously exciting opportunities for applications [3–5]. These materials are usually physically hard and chemically inert which make them difficult to structure by standard top-down technologies, such as optical or e-beam lithography used for subtractive patterning.

Stencil-assisted patterned deposition (often referred to as nanostencil lithography, NSL[6]) is in contrast an additive patterning technique constituting a very promising alternative: only material passing through an opening of a shadow stencil mask close to the substrate reaches the substrate, thus avoiding subtractive patterning steps. The obtained structures share a similar shape to the apertures of the stencil. It has the advantages of being a single step, high throughput fabrication method, allowing parallel processing of a full wafer [7,8]. Structure resolution below 50 nm has been demonstrated [9] and the first devices based on stencil-assisted deposition have been produced [8,10,11].

Stencil deposition is mainly used for the deposition of metals by evaporation, but the technique has also been applied to deposit oxides using Physical Vapour Deposition techniques (e.g. room temperature PLD [12], high temperature PLD [13,14], non reactive magnetron sputtering [15]). In the present work, we combine it with a Chemical Vapour Deposition (CVD) technique, namely Chemical Beam Vapour Deposition (CBVD). This technique is based on Chemical Beam Epitaxy (CBE) and Metalorganic Molecular Beam Epitaxy which arose from the merging of two parent techniques, namely CVD and Molecular Beam Epitaxy [16]. They are vapour phase deposition techniques operated under high vacuum (HV) conditions ($<10^{-3}$ Pa) in which chemical precursors reach the substrate after a ballistic transport from one or several sources and decompose at the heated substrate surface by a chemical reaction. It has been known for more than 25 years that CBE techniques are highly compatible with the use of shadow masks to realize selective deposition [17,18]. Micrometric III–V structures were deposited and their application to integrated laser/waveguide applications [19] was demonstrated. The major problem associated with deposition through stencil masks is related to unwanted deposition on the mask [20,21] resulting in:

- (1) "clogging", which is the modification of the mask aperture size with time due to material deposited on the side walls of the apertures. This process is particularly problematic when the deposited thickness is of the same order as the aperture size as in the case of nanostencils.

- (2) "membrane stability problems". Stencils usually consist of 50–100 nm thick Si or SiN membranes, which are very fragile. They are particularly sensitive to the stress induced by material deposited on top of them, thermal mismatch and eventual interdiffusion. Solutions proposed in the literature include the functionalization of the

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stencil with monolayers that prevent deposition [22] and the incorporation of micro-heaters in the stencil [23]. These solutions are however complicated and limited to some specific deposition processes.

A study discussing the limitations of combining shadow masks with HV-CVD was previously reported before by Reinke et al. [24]. However, in that case the mask was effectively a structured substrate that required etching to fabricate and a subsequent lift-off step to remove, after completion of the HV-CVD process.

In this work, we present results of micro-feature growth with stencil mask definition in an advanced CBVD tool. It exhibits several improvements and offers increased flexibility as compared to previous CBE reactors. It contains a precursor delivery unit based on the geometrical distribution of many point sources around the substrate, enabling the generation of independently controlled flow gradients for different precursors across the substrate [25]. As a consequence, it enables the growth of complex structured oxide films, using a stencil mask, in one step. In the case of a chemical deposition process involving the chemical reaction of a precursor molecule, the deposition rate depends on substrate temperature when working in the reaction limited regime. We shall show in this paper that the introduction of a gap between substrate and mask may enable for a high enough temperature difference between the two parts to avoid deposition on the stencil. The gap can be kept small enough to minimize the "blurring" effect, which is a widening of the deposited pattern dimensions compared to the stencil aperture size, and originates both from a geometrical factor and from the diffusion of chemical precursor molecules that can decompose between mask and substrate at the edges of the structure. Additionally, the mask–substrate gap allows the fabrication of complex 3D structures by superposing deposits from several precursor beams passing through the same mask aperture. Finally, the problems of clogging and membrane instability are alleviated by eliminating deposits on the mask, resulting in potentially limitless mask reusability.

2. Experimental details

2.1. Deposition system

A Sybilla 150 Chemical Beam Vapour Deposition system (already described elsewhere [25,26] and presented schematically in Fig. 1) was used to deposit titanium oxide.

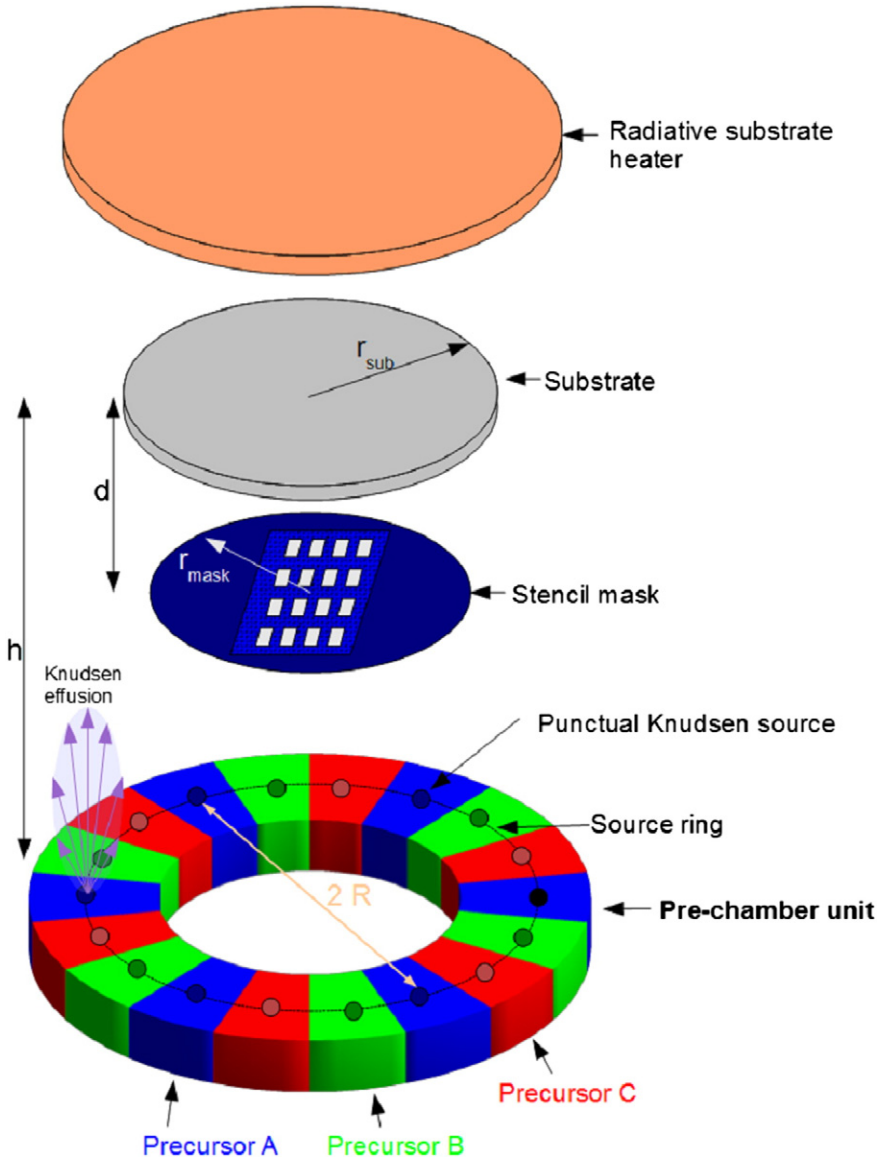

Fig. 1. Principle of the Chemical Beam Vapour Deposition system. Source–substrate distance: h = 14.7 cm, source ring radius: R = 11.5 cm, substrate radius: r_{sub} = 2 inch, mask radius: 2 inch, mask-substrate distance: d = 30 to 100 μm.