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Direct patterning of complex oxides by pulsed laser deposition through stencils

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Abstract. The possibilities to grow isolated structures of complex oxides by pulsed laser deposition through stencils were investigated. A stencil consisting of a SiN membrane with apertures of several hundred nanometers embedded in a Si chip is placed in front of a heated substrate (up to 750 degrees Celsius). Deposition through these apertures results in resistless, direct patterning by local deposition of complex oxides like ferroelectric Lead Zirconate Titanate. The created isolated structures were analyzed by AFM imaging. Under-deposition, in this work called broadening, is inevitable during stencil deposition and is depending on deposition parameters, especially pressure. Different causes of broadening are mapped and discussed.

1. Introduction

Patterning of thin films is usually a process consisting of many processing steps like spincoating photoresist, UV-illumination and chemical or ion-etching. Although this approach contains many steps, it works well for many materials like metals, their oxides and semiconductors but complex oxides are not easily structured by these conventional techniques. Complex oxides can be obtained with a broad range of properties and all have in common that temperature and oxygen pressure during thin film growth have to be high (>500 °C and ~0.1 mbar). The chemical stability of many of these oxides prevents structuring by wet-etching. Patterning by (reactive) ion etching often induces defects in the oxides (e.g. oxygen vacancies) resulting in damaged and leaky structures. Furthermore, the high temperatures make lift-off process using photoresist impossible. In case of stencil deposition, a direct copy of the structures in the stencils is made by depositing through the apertures of the stencil. The local deposition obtained in this method enables structuring materials in one deposition step and moreover structuring complex oxides at high temperatures without further etching steps [1,2].

Many new versatile surface patterning techniques are being developed, like nanoimprint lithography, soft-lithography and nano-dispensing. Stencil deposition is one of these promising techniques and has several advantages. As mentioned above, it is a resistless technique which reduces the number of processing steps and it has the possibility to create millimeter sized combined with nanometer sized features in one deposition run. For instance nanometer sized features can be combined with macro sized wiring in one deposition run. No chemical treatment is needed, making it also suited for deposition on vulnerable surfaces like biomolecules or self-assembled monolayers (SAM's) [3].

Pulsed laser deposition (PLD) is one of the few techniques satisfying the necessary deposition conditions for complex oxides growth. The ability to use heated single crystal substrates even enables epitaxial growth of these materials. We applied stencil technology in structuring ferroelectric $PbZr_xTi_{1-x}O_3$ (PZT). This material has become increasingly interesting in, for example, data storage applications, like FE-RAM. High throughput direct patterning techniques like stencil deposition for this material is therefore essential. Up till now all research on stencil depositions [1,4,5] have been done at room temperature but the combination of high temperature and direct patterning makes this technique really distinct and will be presented in this paper.

2. Experimental

Stencils used in this study consist of 1 μm thick SiN membranes embedded in a silicon chip. SiN is deposited by chemical vapor deposition to obtain a low stress film to prevent it from rupture. Structures are created by standard photolithography techniques or laser interference lithography, in which the latter can only create regular arrays of, for instance, circular or elliptical patterns. Structures in the photoresist are transferred by reactive ion etching followed by a KOH wet back-etch to create the free standing membrane. The stencil production process is described in more detail by van Rijn et al. [6]. A SEM image of the stencils used most in this research and a schematic drawing of a mask deposition are shown in figure 1. The aperture dimensions are 0.7x3 μm^2 with a minimum separation of 0.7 μm and a maximum separation of 1.9 μm.

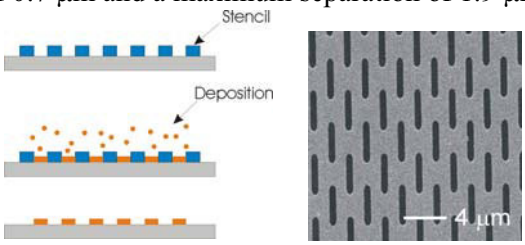

Figure 1. Schematic drawing of a stencil deposition (left), and SEM image of 1 μm thick SiN membrane showing the apertures (right).

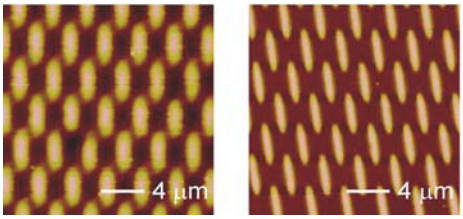

Figure 2. AFM image of platinum deposited on a silicon substrate for the stencil in contact (left) and a separation of 20 μm (right). The laser fluence was 5 J/cm^2, at frequency of 10 Hz for 10 minutes and the target-substrate distance was 40 mm.

The PLD system consists of a KrF laser (248 nm) with FWHM pulse duration of ~25 ns. The vacuum system is turbo-molecular pumped and has a typical base pressure of 10^{-7} mbar. The laser beam is focused onto a rotating target with the substrate mounted onto a heater opposite of this target. For epitaxial growth studies, depositions were done on single terminated $SrTiO_3$ (STO) substrates. This is obtained by treatment of the substrate, consisting of cleaning in acetone and ethanol after cutting to remove wax and other impurities, water treatment, buffered-HF etching and annealing. This results in TiO_2 terminated and atomically smooth surfaces of the substrates [7].

The stencils are glued on a, for this research designed, holder for experiments where the gap between stencil and substrate can be varied. The holder can be moved with respect to the substrate by adjusting three micrometer screws. For high temperature experiments, stencils are glued with silver-paste onto a stainless steel plate and put into contact with the substrate. In this contact method, the gap cannot be controlled and even in this hard contact, the gap is estimated to be in the order of a micron. Deformation of the stencil can occur as a result of high temperature depositions and differences in thermal expansion coefficient. A membrane can become fragile depending on the deposited material.

3. Results and discussion

In the most ideal situation for stencil deposition the width of the deposited pattern equals the aperture dimensions in the stencil. Substrate temperature and ambient gas pressure can result in deviation from these dimensions. For room temperature depositions at moderate pressures (~ 10^{-2} mbar), the structure

broadening can be less then 50 nm. Under these conditions, depositions were done with variable gap on room temperature silicon substrates. Up to a separation of 20 μm a clear copy of the structure in the stencil was obtained. Broadening of more then 10 μm is observed when the gap is larger then 60 μm. When put into hard contact, deformation of the stencil results again in excessive broadening. The deposited structures for hard contact (FWHM 2 μm) and a gap of 20 μm (FWHM 700 nm) are shown in figure 2. Since the spotsize of the focused laser beam is in the same order of the membrane size in the stencil (several mm^2) and the target-substrate distance is much larger, in the range of 50 mm, geometrical broadening can be discarded. This is demonstrated by the little broadening at a gap of 20 μm. The broadening at a gap of 60 μm (not shown) is a result of interaction between particles behind the stencil inside the plasma with a relative high pressure.

Typical PLD parameters for the deposition of PZT thin films are a substrate temperature of 600 °C and a background oxygen pressure of 0.13 mbar. When depositions are done for PZT under these conditions the broadening is extreme, as shown in figure 3 a), where it is in the order of several micrometers. There is a 10 nm thick film completely covering the surface of the substrate and only little structure (height ~ 1 nm) can be seen. Some broadening at higher substrate temperature can be expected [8,9] but this can not explain the broadening observed in these experiments. Figure 3 b), c) and d) show isolated structures obtained by depositions done at different pressures, 0.013, 0.05 and 0.1 mbar of oxygen, respectively. Between 0.1 (figure 3 b)) and 0.13 (figure 3 a)) there is a sudden transition to extreme broadening. Shockwave formation as a function of pressure is also a very abrupt transition, linking this broadening to the formation of a shockwave. At the pressures used, a shockwave, typical for PLD, can be formed by deceleration of the leading edge of the plasma plume due to collisions of the expanding plasma in the static background gas. The pressure behind the leading edge will rise and can be up to a factor of four [10] higher than the ambient gas pressure. Shockwave expansion will continue until the pressure inside the shockwave is equal to the ambient gas pressure, followed by diffusive propagation. A stencil placed in front of a substrate with a certain gap acts as a division between a volume of high pressure from the shockwave and a volume of low pressure in the gap. The propagating material experiences a pressure gradient resulting in excessive broadening.

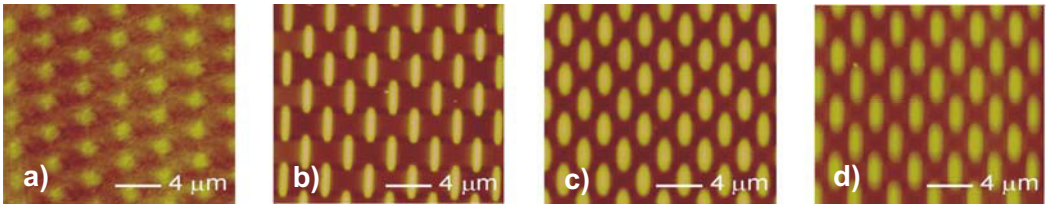

Figure 3. Depositions of PZT done at 400 °C for a) 0.13 mbar, b) 0.013 mbar, c) 0.050 mbar and d) 0.1 mbar oxygen background pressure. The laser fluence was 2.5 J/cm^2, at frequency of 2 Hz for 45 minutes and a target-substrate distance of 58 mm.

For successful stencil deposition a complete understanding of all broadening mechanisms is needed. Figure 4 shows an overview of several mechanisms that came up during this research. The most ideal case for a stencil deposition is shown in a) and holds for deposition techniques with low number densities and highly directional low energy evaporated material expanding in low background pressures. If the size of the evaporation source is much bigger or smaller, geometrical broadening will occur as shown in b). High substrate temperatures will increase surface diffusion (figure 4 c)) and therefore the amount of broadening. Surface diffusion will also be increased by lowering the pressure. Subsequently, it increases the kinetic energy of the arriving species, inducing higher surface diffusion. A moderate increase of the pressure results in sharper structures. Collisions between plasma and background gas at even higher pressure lead to more diffusive propagation and, as a result, increased broadening. Surface diffusion strongly depends on the deposited material. For example, during

deposition of strontium ruthenate (SRO) under the same conditions mentioned above, even more broadening is observed. Next to these mechanisms, a shockwave can be formed resulting in extreme broadening as shown in d).

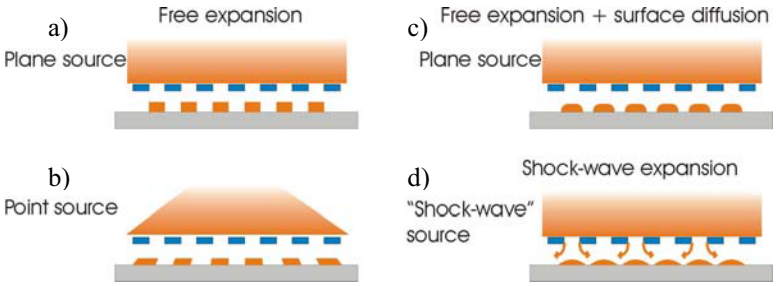

Figure 4. Several causes of broadening during stencil deposition. The amount of broadening depends on the gap between stencil and substrate.

4. Conclusion

Stencils have been successfully used in the direct, resistless patterning of complex oxides. Materials like PZT and SRO have been deposited by PLD under typical growth conditions. The SiN membrane in the stencil can withstand the high temperatures needed (up to 750 degrees), although differences in thermal expansion coefficient can make the stencils fragile. Several causes of broadening have been mapped showing the importance of the oxygen background pressure on successful deposition of complex oxides structures. Excessive broadening is observed under the typical conditions for complex oxide deposition. High background pressures result in the formation of a shockwave which results in this excessive broadening. Structures can be isolated deposited by tuning the gas pressure below this shockwave formation threshold. New experiments involve the creation of all-oxide ferroelectric memory elements by stacking SRO/PZT/SRO and deposition through smaller apertures.

Acknowledgements

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