REACTIVE OXIDE MICRO MOLDING OF DIFFRACTIVE OPTICAL ELEMENTS IN GLASS AND TRANSPARENT CERAMICS

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ABSTRACT

We present a new chemical process that we call **'Reactive Oxide Micro Molding' (ROMIM)**, for the realization of micro-optical components in glass and transparent, high dielectric ceramics for Micro-Opto-Electro-Mechanical System applications. The technology is based on an original chemical route to prepare a stable solution of reactive oxide nano-particles and reactive oxide-oligomer units at very high concentration. Thermal processing triggers a reactive agglomeration amongst these reactive species without causing defects and cracks, thanks to both the high density of the solution and the absence of organic material. The final result is a pure glass or ceramic structure without inclusion of organic materials.

1. INTRODUCTION

Diffractive Optical Elements (DOE) are essential for many Micro-Opto-Electro-Mechanical Systems (MOEMS) applications and are being used in integrated optics, quantum electronics, holography spectroscopy, etc. Presently, X-ray and e-beam lithography are used to fabricate diffractive optical elements in Si and polymeric materials on the nanometer scale [1-3]. Polymeric materials are the better choice, as they are transparent in a broader wavelength region, but, they suffer from several disadvantages like a large thermal expansion coefficient, limited mechanical strength and degradation with time under illumination. The best optical materials for MOEMS applications are glass and transparent ceramics [4-8]. However, their microstructuring is a real challenge owing to their high resistance toward chemical and mechanical erosion. One possible way to micro- or nano-structure glass/ceramics is the direct casting from a liquid solution. However, melt molding is not easy because of the very high melting point, higher than many mold materials.

The present study provides a solution to this problem, by using a liquid solution of reactive oxide units. We name this technique **ROMIM**, since it employs micro-molding using reactive oxide-particles and reactive oxide-oligomer units. This technique is neither an ORMOCER sol-gel technology, which is based on materials containing both organic and inorganic components [9], nor a UV sol-gel technology that employs photolithography to fabricate microstructures of silicon-organic polymer materials [10]. It is a unique micro-molding process completely different from 'Micro Molding in Capillaries' (cannot be used for closed structures like a Fresnel lens) and 'Solvent-Assisted Micromolding' (employs particles dissolved in an easily evaporating solvent) [11].

2. TECHNOLOGY

We use a chemical process, as illustrated in figure 1, to generate nano-size reactive oxide particles and reactive oxide-oligomer units without employing long chain polymers and surfactants, while maintaining the oxide particle size and their reactivity in solution. This results in shrinkage of less than 2-3 % during agglomeration.

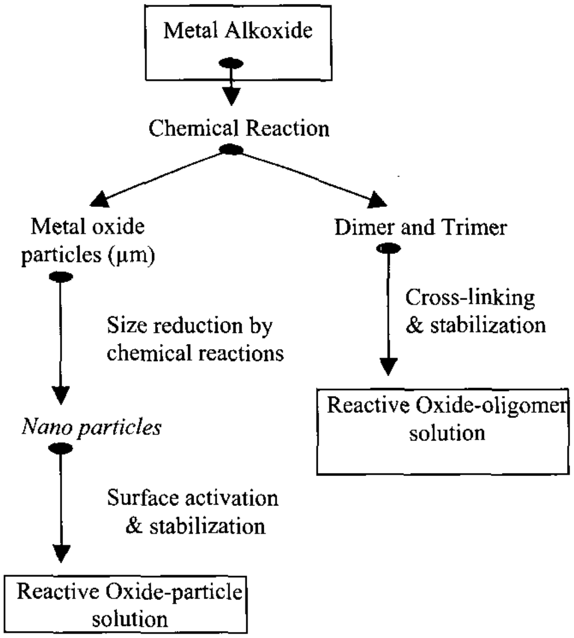

Figure 1: Preparation of reactive oxide particles and oligomer solution by controlled multi-step chemical reactions employing metal alkoxides as precursors.

The **ROMIM** process involves two main steps: (i) transfer of a (silicon or polymer) master micro/nano-structure to a soft polymer and (ii) the coating of the latter

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with reactive oxide solution (Figure 2). The structure is dried and removed from the soft polymer. Subsequently, it is subjected to further heat treatments, leading to pure glass/ceramics nanostructures.

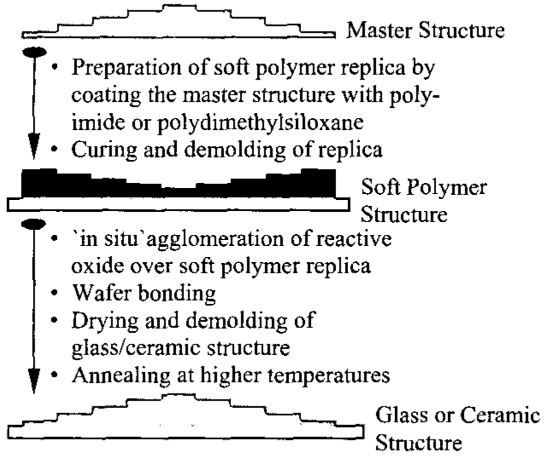

Figure 2 : Descriptive view of the ROMIM process: a master structure is first used to prepare a negative replica in a soft -polymer and subsequently this replica is used to prepare a pure glass / ceramic structure employing reactive oxides.

3. RESULTS AND DISCUSSION

We have realized glass (silicon oxide) and transparent ceramics (titanium oxide and zirconium oxide) nanoscale optical structures, like diffractive gratings and Fresnel lenses. Figure 3(a) and 3(b) show grating structures realized in silicon oxide. These photographs reflect a glass microstructure with a roughness in the nanometer range only. A diffraction pattern of the crossed grating structure, under the illumination of 634 nm laser light, is shown in figure 3(c). The calculated diffraction intensity profile of the crossed grating is shown in figure 3(d). The diffraction pattern, showing higher order peaks of high intensity, are characteristic for a good replicated structure. These silicon oxide gratings were replicated using a solution containing small oligomer units of silicon oxide prepared through hydrolytic-polycondensation of silicon alkoxides. These oligomer units have hydroxyl groups that promote intra- and inter-oligomer chain bond formation and hence complete silica network formation on heat treatment at an elevated temperature. Shrinkage in this case is minimum, compared to conventional sol-gel processes, as all the reactive hydroxyl groups are in close proximity, being stabilized by a proper combination of protic-aprotic solvent.

The titanium oxide solution to fabricate transparent ceramic material microstructures having high

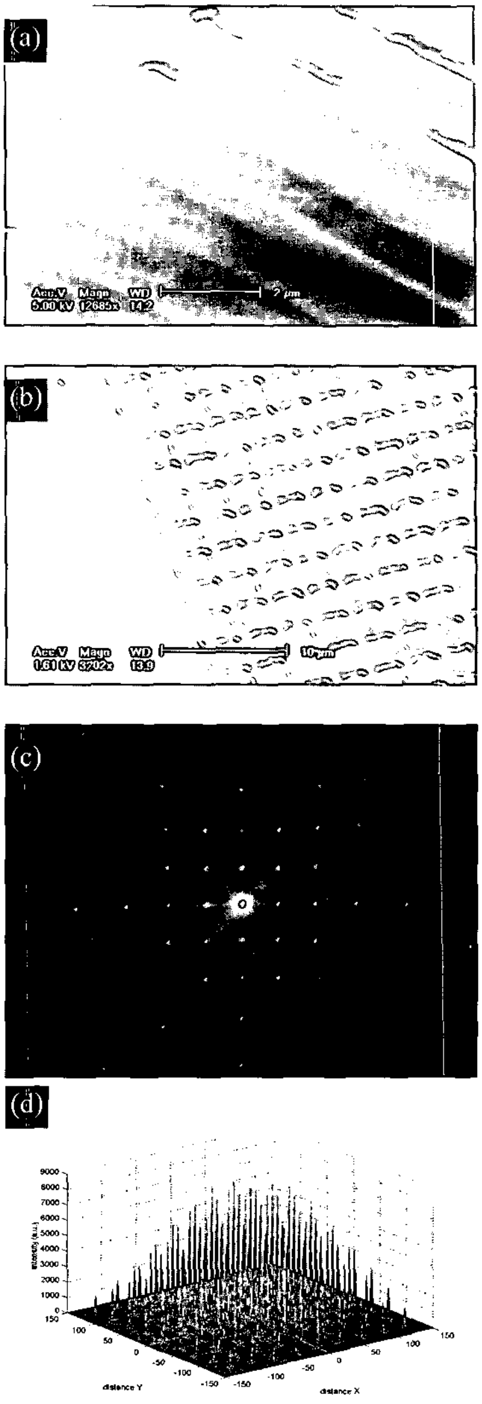

*Figure 3 : SEM photographs of (a) a line grating, (b) a crossed grating structure realized in **silicon oxide** and (c) its diffraction pattern and (d) calculated intensity profile of diffraction.*

refractive index, contains nanoparticles of TiO_2 and $TiO(OH)_2$, a chemically active aqua complex of titania, which helps in the binding of titanium oxide units during annealing. Figure 4(a) and 4(b) show SEM photographs of a replicated Fresnel lens in transparent *titanium oxide*, which is just impossible to prepare by any other available technology. The lines observed in fig. 4(b) perpendicular to the proper ridges of the Fresnel lens are the consequence of the use of a polymer master structure, which has been prepared by sequential e-beam writing. Fig. 4(b) shows a detail where the depth of the structure of the Fresnel lens changes, demonstrating that different aspect-ratio structures can be realized in a single molding step; fig. 4(c) is a first optical characterization of this structure, showing the ability of the Fresnel lens to generate a wide beam with satisfactory uniformity.

The most difficult oxide to replicate is zirconium oxide. It does not form any reactive species in a solution and, moreover, the gelling time is only a few minutes if it is to be prepared through a conventional sol-gel route. Therefore, we prepare a reactive oxide solution by giving nanoparticles of zirconium oxide a chemically active coating stabilized in an aprotic solvent. This coating material, which is a zirconium oxide precursor, forms chains amongst zirconium oxide nanoparticles upon heating and binds them very well without causing major shrinkage problems. Figure 5(a) shows a linear grating

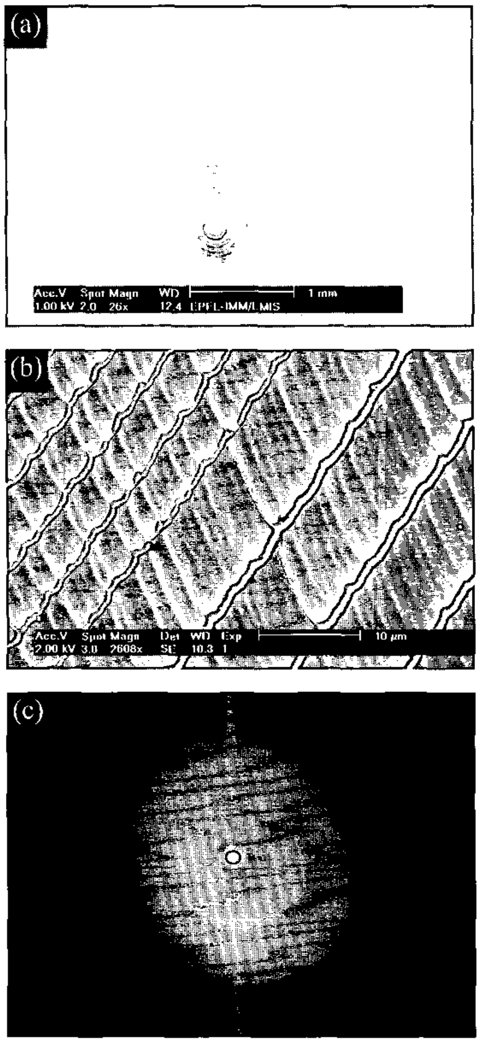

Figure 4: SEM photographs of (a) a Fresnel lens in ***titanium oxide*** *, (b) a detail showing that different heights can be realized in a single molding step and (c) a refractive image under laser irradiation at a distance of 300 mm; the diameter of the spot is 80 mm.*

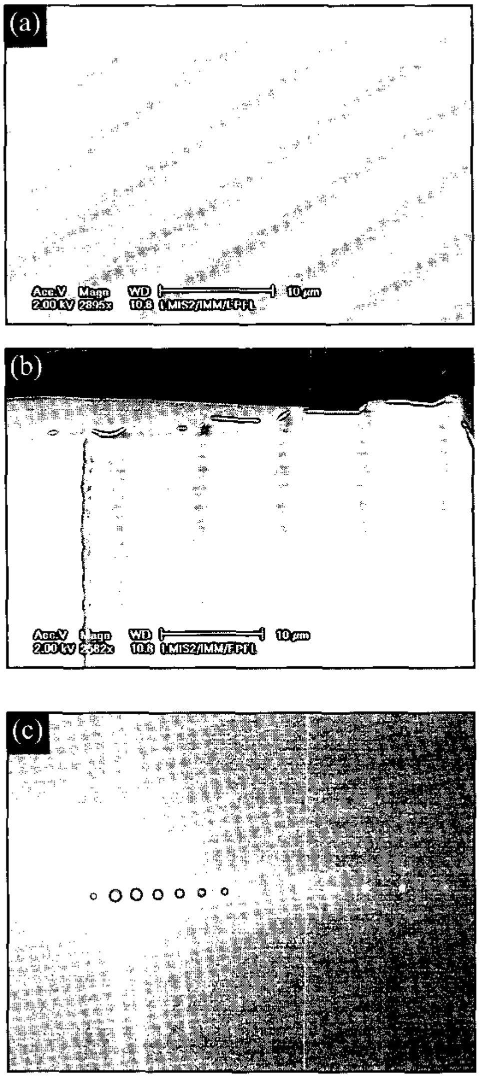

Figure 5 : SEM photograph of (a) a linear grating structure in ***zirconium oxide,*** *and (b) an oblique view of a detail of the profile; (c) is the corresponding diffraction pattern under 634 nm laser illumination .*

structure realized in zirconium oxide. An oblique view, to show the depth profile of the grating, is shown in figure 5(b). Again, lines due to the e-beam writing of the master structure are visible. The optical characterization of this linear grating using 634 nm laser light is shown in figure 5(c). One expects to find a horizontal linear array of spots for a perfect linear grating structure. The continuous vertical lines in figure 5(c) are a consequence of the laser beam writing process of the master structure. Looking at the detailed view of fig. 5(b) (and also 4(b)), one indeed observes that the line writing process results in a certain roughness perpendicular to the actual grating structure, giving rise to a broad reflection angle in the vertical direction of figure 5(c).

4. CONCLUSION

We have presented a new chemical process that we have called **'Reactive Oxide Micro Molding' (ROMIM)**, for the realization of micro-optical components in pure SiO_2 glass and transparent, high dielectric ceramics, like TiO_2 and ZrO_2. The technology is based on an original chemical route to prepare a stable solution of reactive oxide nano-particles and reactive oxide-oligomer units at very high concentration and is the only available method today to realize ceramic TiO_2 and ZrO_2 micro/nano-structures in a simple replication process. We anticipate that our technology will have great potential for the manufacturing of integrated optical devices, employing lenses and sub-micrometer diffractive optical elements.

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