

I. Deliverable: Report on the photoinitiated CVD of molecular glass low k materials with optimized morphology

Task ID : 425.017

Task Title : Environmentally Benign Vapor Phase and Supercritical CO₂ Processes for Patterned Low k Dielectrics

II. Summary

Photo-initiated CVD (piCVD) is employed as novel approach for additive patterning of thin film structures. A free radical generating photo-initiator, such as benzophenone (BP), or its derivative Michler's Ketone (MK), is first patterned onto a substrate using microcontact printing. This substrate is then exposed to UV irradiation in the presence of a vaporized monomer in a process termed photo-initiated CVD (piCVD). The only requirements for the monomer to be subsequently polymerized upon exposure to UV irradiation are that it have an appropriate volatility to enter the vacuum system and that it possess one or more vinyl bonds. One such monomer is trivinyltrimethylcyclotrisiloxane, a molecular glass with three vinyl groups. The film formed is in the organosilicate gas (OSG) category of low k materials. The additive piCVD growth of a second, model monomer having a single vinyl group, cyclohexyl methacrylate (CHMA) was also explored. This choice was motivated by that fact that pCHMA is an excellent sacrificial material and patterned films of this polymer have been utilized in the formation of air gap structures, with air being the ultimate low k material ($k=1$).

Traditionally, the creation of patterned thin films has been performed by subtraction, requiring the deposition of full layers of material which are then selectively removed to create the desired structures. Often an additional photoresist layer, which can be patterned through UV irradiation, must also be deposited. Further steps are also required to develop the resist, transfer the pattern through the resist to the material below, and then remove the remaining resist. This process is slow, wasteful, and environmentally unfriendly due to the large volumes of solvent involved. In addition, a plasma etch process is often utilized in pattern transfer which can result in damage to both deposited structures and the underlying substrate. The additive patterning approach described in this report requires fewer steps and is quite general. Thus, it would allow deposition of patterned films of any material that can be synthesized by piCVD.

III. Technical Results and Data

Experimental

Experiments designed for creating additively patterned piCVD films were performed through microcontact stamping of either benzophenone (BP) or Michler's Ketone (MK) dissolved in acetone. These species are type II free radical initiators which can be activated with both 254 and 365 nm wavelength UV photons. In addition, the low vapor pressure of these initiators (< 3 mtorr at 298 K) allows samples to be placed under vacuum without expectation of initiator pattern evaporation. Multiple initiator concentrations were examined, although best results were generally obtained at the highest possible (saturation) concentration. Initiator solutions were applied to the surface

of a PDMS stamp using a cotton swab. The stamp was either immediately contacted to the deposition surface or first dried completely with room temperature nitrogen. All depositions were performed on silicon wafer substrates. These wafers were either utilized without modification or surface modified with trichlorophenylsilane, for the surface presentation of phenyl groups, prior to initiator stamping.

Figure 1 displays representative results of the patterned layer resulting from piCVD on unmodified substrates to which a microcontact stamp, wet with a BP-acetone solution, was applied without nitrogen drying of the stamp. Some patterned polymer growth is evident, although the regions of growth only correspond to the outline of the microcontact stamp feature. This phenomenon, observed in inkjet printing of microscale features is commonly termed the 'coffee stain' effect. It is the result of the BP solution concentrating during evaporative drying of the acetone. Retention of pattern edge fidelity occurs due to surface tension and wetting effects which dictate that the evaporative front move from the center of the wetted area to the edge. The intentional use of this phenomenon to create patterns, known as edge transfer lithography (ETL), has been shown to allow the transfer of smaller features than traditional microcontact printing. However, while depositions on substrates patterned with BP in this manner do create line features of 2-3 μm in width, as shown in Figure 1b, the process is not highly reproducible, as evidenced by the lack of regularity of the pattern in Figure 1a.

It should be noted that no deposition was observed when the microcontact stamp was dried with nitrogen prior substrate contacting. Instead, crystallization of BP on the surface of stamp was apparent. BP is a highly crystalline solid at room temperature, and the formation of large BP crystals on the face of the stamp likely prevented the transfer of any initiator to the substrate. This phenomenon occurred regardless of whether or not the substrate was modified with trichlorophenylsilane.

Figure 2 displays an optical micrograph of the patterned deposition resulting from the piCVD on a trichlorophenylsilane modified substrate to which a microcontact stamp, wet with a MK-acetone solution at a saturation concentration of 2.2% by weight, was applied after drying with nitrogen. Patterned deposition is now observed over the full area. It is theorized that by utilizing a solution of MK in acetone at saturation, the initiator was forced to precipitate on the stamp surface during solvent evaporation. This led to complete coverage of the stamp area with MK, which then transferred to the substrate during contacting due to favorable interactions with phenyl modified surface. Experiments following the same stamping procedure on an unmodified substrate resulted in no material deposition, validating the assumption that the presence of phenyl groups on the substrate surface aides in the transfer of the initiator from the microcontact stamp.

It should be noted that the features shown in Figure 2a have a thickness of 25-30 nm, as measured by profilometry. Many applications of patterned thin films, especially those in the microelectronics industry, require significantly larger film thicknesses. In order to achieve thicker patterned films on a reasonable time scale, deposition rates need to be at least an order of magnitude higher than the 0.5 nm/minute observed. One common approach for increasing film growth rates in iCVD is to increase the partial pressure of the monomer within the deposition chamber. This in turn increases the surface concentration of adsorbed monomer and therefore the rate of polymerization. However, when monomer pressure is increased from 250 mTorr to 300 mTorr under 254 nm UV illumination, patterned film growth is no longer observed. Instead, a continuous

film was deposited on the substrate, with no observable differentiation between areas patterned with photo-initiator and those without. It is theorized that the higher surface concentration of the monomer allowed for auto-polymerization under the 254 nm UV irradiation. To avoid this issue, the wavelength of irradiation was increased to 365 nm. This less energetic wavelength, while still activating the MK present on the surface, did not initiate auto-polymerization of the monomer even at a partial pressure of 300 mTorr. This allowed the deposition of patterned films with 25 μm features at thicknesses of 250-300 nm, as measured by profilometry, as displayed in Figure 2b.

Conclusions

In this work, the additive patterned deposition of thin piCVD films from a microcontact printed photo-initiator has been demonstrated. Utilization of this patterning technique was shown to require transfer of photo-initiator from the stamp surface by preventing initiator crystallization and optimizing surface preparation. Patterned deposition required the use of a reduced energy UV wavelength, 365 versus 254 nm. Future work with this technique will focus on alternate lithography approaches, such as photo-bleaching of a blanket initiator layer through interference lithography, for the creation smaller patterned features.

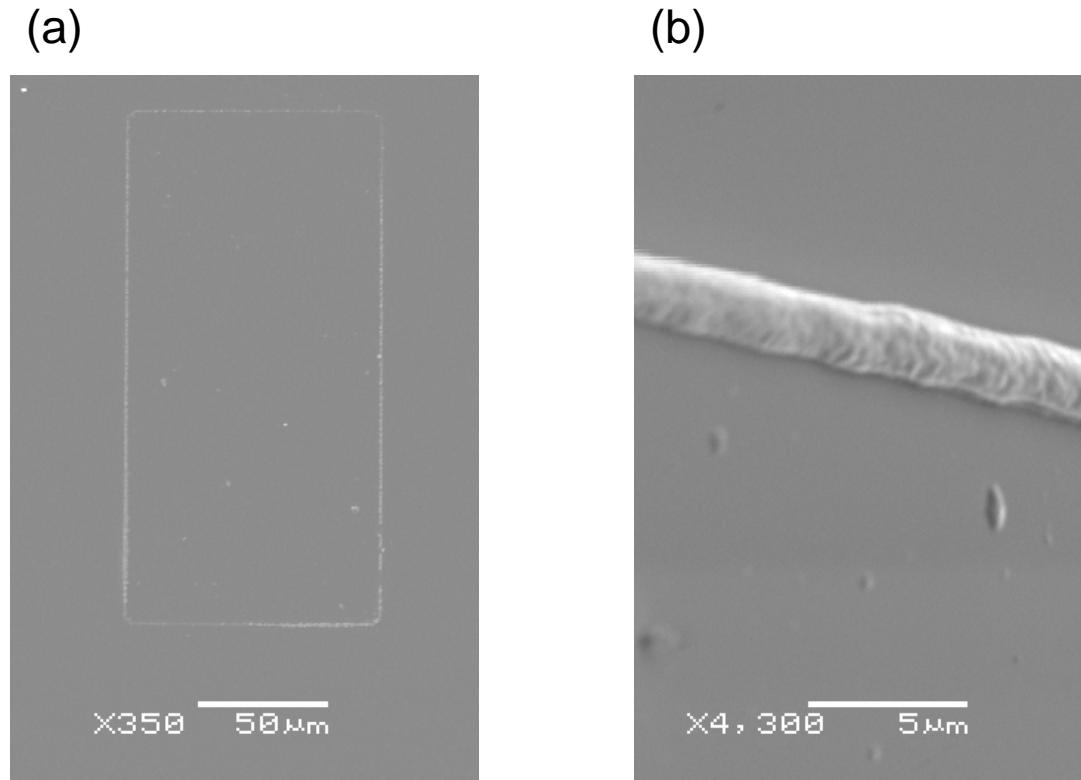


Figure 1. Scanning electron micrograph showing patterned piCVD following microcontact printing of BP/acetone solution. (a) depicts the outline of a 100 μm X 200 μm rectangle resulting from concentration of the BP at the edge of the feature as the acetone evaporated. (b) shows an enlargement of one edge of the deposited structure.

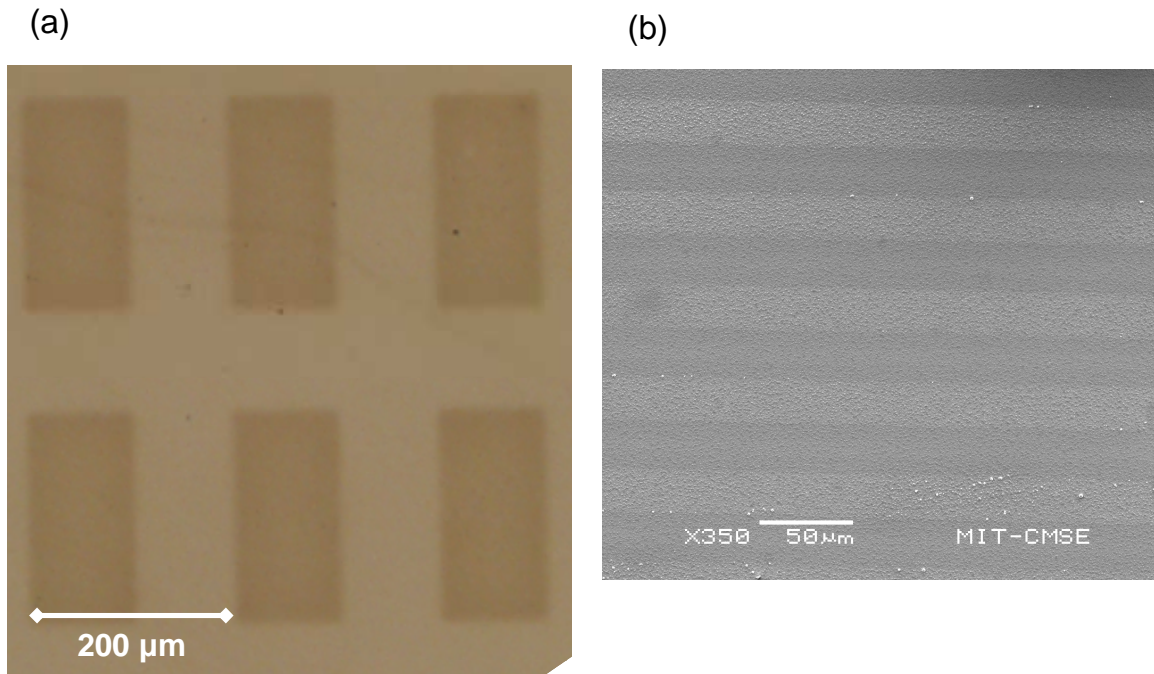


Figure 2. (a) Optical micrograph of $100\ \mu\text{m} \times 200\ \mu\text{m}$ features deposited through piCVD from microcontact patterned MK initiator. Full feature area is filled in while deposition is not apparent outside of initiator patterned area. (b) SEM of $25\ \mu\text{m}$ lines and spaces deposited to a film thickness of $\sim 250\ \text{nm}$.

IV. Supplementary Materials Available

_3_Related Publications

O'Shaughnessy WS, Gao ML, Gleason KK. "Initiated chemical vapor deposition of trivinyltrimethylcyclotrisiloxane" *Langmuir* 2006, 22, 7021-7026

W. Shannan O'Shaughnessy, Sal Baxamusa, and Karen K. Gleason, "Additively Patterned Polymer Thin Films by Photo-Initiated Chemical Vapor Deposition (piCVD)" *Chemistry of Materials* 2007, 19, 5836-5838