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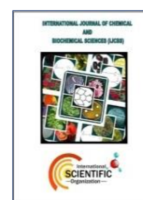

Resistless nano-etching of UV-irradiated vinyl-functional silsesquioxane thin film by alcohol-alkaline solution

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Abstract

Defining optical thin film-based components such as waveguides, microlens, etc. typically encounter dimensional-based challenges especially when it comes to nano-dimensional features processing. This work focused on the optimization of wet etching process on the photosensitive organic-inorganic thin film in which desired pattern from UV-exposed photolithographic technique was successfully defined. Dissolution of the non-exposed areas was performed using a mixture of alcohol-alkaline solution and parameters such as concentration of etchant and etching time have been studied for the impact on morphology, topography, and optical properties. The optical properties of film thickness indicated that the non-exposed areas experienced thickness loss with low etchant contributed to the steady-state thickness reduction than the higher concentration of etchant used, whereas the refractive index is maintained throughout the process. Changes in topography properties indicated that surface features of arithmetical surface mean height, Sa exhibited that film smoothness and textural gross shapes are greatly enhanced by the combination of composition of etchant ions and etching duration.

Keywords: Thin film, organic-inorganic, wet etching, UV micro-patterning

Full length article **Corresponding Author*, e-mail: tamizi@sirim.my

1. Introduction

Recently, optical waveguides have been widely produced by various 'hard' deposition techniques such as flame hydrolysis deposition (FHD), plasma enhanced chemical vapor deposition (PECVD) etc. [1,2,3]. On the other hand, sol gel technique which employed chemical synthesis route offers more rapid and less expensive production cost that has been the most important issues for the waveguides fabrication industries [4,5]. However, both 'hard' deposition techniques and conventional inorganic based sol gel method still require photoresist deposition as masker during photo-lithographic process to define pertinent microscopic architectures of the pattern [6,7]. Photoresist consists of high molecular weight polymer e.g. resin, usually give rise to contamination on the pattern and the solvents they used to it place severe compatibility restrictions on the substrate [8]. Therefore, many researchers have been developing novel materials and processes for the photoresist and mask reduction in photolithography [9-13]. Apart from that, etching techniques such as wet etching and reactive ion etching (RIE) also play important role in defining the pattern by contributing multiple steps [14]. This work focuses on the optimization of the wet etching process using NaOH alkaline solution on the silica based organic-inorganic hybrid sol gel thin film in order to define optical components.

2. Materials and methods

2.1. Materials

This study investigates various wet etching composition in order to define the pattern formed on the irradiated photosensitive thin film. Composition for wet etching was altered based on the solubility of the selected materials within the film matrix [15,16]. In this research, a composition of sodium hydroxide (NaOH) and ethanol (EtOH) has been selected as etching solution. NaOH is chosen as the major etchant ions based on its capability to dissolve most glassy materials especially silica. Short alkyl group alcohol such as ethanol is chosen because of it's superior dissolution of short chain polymers properties. The etching process has been executed on the silsesquioxane thin film that previously irradiated under UV light with the presence of negative type optical waveguides pattern photo mask that consists of UV-irradiated and non-irradiated areas

[17]. The technique applied in this etching process is by means of flipping immersion where a thin film sample is immersed in 150mL etchant solution and then flipped up and down for certain period of time.

2.2. Physicochemical characterization

Morphology studies of the etched pattern from UV treated photosensitive thin films are examined by microscopic techniques. Reflective light microscope is used to inspect the early development of patterned structures immediately after etching process. Field Emission Scanning Electron Microscopy (FESEM) is used to gain in-depth view of the developed patterned profile at higher magnification. The physical surface properties such as surface roughness are characterized by using Atomic Force Microscopy (AFM). The morphology study is also complemented by an analysis of the film thickness during the etching process. Wet etching does not only affect the morphology of the thin film but also the film thickness. Changes in film thickness with etching process are monitored using spectroscopic reflectometer in the range of 400 to 1000 nm.

3. Results and discussion

3.1. Elongation of Etching Time

Micro-patterning involving UV light irradiation has been applied on the thin film with presence of negative type photo-mask. It promoted organic cross-linked network by undergoing addition photo-polymerization C=C double bonds of vinyl groups. Such polymerization also densified the irradiated area and increased refractive index. Pattern for optical channel from photosensitive thin film was obtained by leaching with a mixture of alcohol-alkaline solution. Composition of etching solution used consist of NaOH:EtOH:H_2O with a volume ratio of EtOH to water at 10:25 and NaOH concentration is varies between 1 to 5%. Scanning electron microscope images in Fig. 1 showed well defined and smooth pattern profiles formed on the sample irradiated with UV light in the presence of negative type photo-mask. Non-irradiated area was completely dissolved and removed by etching, whereas no significant decrease was observed for irradiated area after etching. This suggests that the UV-irradiated area has high chemical durability against the alcohol-alkaline etching solution due to the densification facilitated by addition photo-polymerization. The emerged pattern from the wet etching process is rectangular in shape with channel width of about 30.0 μm. This product confirms with the pattern of photo-mask used. Observation on film surface after 15s of etching process indicates that all etching solutions exhibit affinity to etch out the non-irradiated areas except for the control etching solution with 0% NaOH. Etching thin films in less than 15s showed incomplete etching process where non-irradiated areas are not fully dissolved into the etching solution as depicted in Fig. 2(a). The etching process time has to be limited to 30s due to the developed optical channel is easily peeled off from substrate as shown in Fig. 2(b). Based on the observation above, the time for etching process in this study is narrowed in between 15 to 30s in order to achieve fully etching of non-irradiated areas without peeling off the UV irradiated areas as in Fig. 2(c).

3.2. Effects on surface morphology and topography

Etching solution compositional effects on the morphology and topography of the etched pattern was investigated by using different concentration of NaOH. A series of etching solution with 0, 1, 2, 3, 4 and 5 % NaOH were prepared by dissolving NaOH pellets in subjected 10:25 volume of ethanol and de-ionized water. Higher NaOH content of more than 5% leads to uncontrolled sample contamination due to re-deposition of NaOH on the surface as shown in Fig. 3. The effects of NaOH concentration on the surface morphology of the sample is investigated after completion of the etching process.

Surface roughness has increased significantly with etching process, from an average of 1.25 nm for film surface before etching to as high as 3.20 nm after etching within different time and NaOH concentration as depicted in Fig. 4. Averages surface roughness by areal, Sa of the irradiated areas for vinyl-silsesquioxane thin film with different NaOH concentration is tabulated in Fig. 5. An overall view on the surface roughness on the samples etched with different concentration of NaOH indicated that longer etching time promoted an increment in surface roughness. This observation is parallel with the nature of etching process in which a longer etching time facilitated more chemical reaction to occur.

Fig. 5 also shows that solution with 1% NaOH produced the highest surface roughness values ranging from 3.065 nm to 3.199 nm within a time frame of 15 to 30s of etching. This is then followed by 5%, 4% and 2% NaOH concentration. Solution that consists of 3% NaOH showed lowest values in surface roughness. Following from this result, it is clear that etching process is active at low NaOH concentration of 1%. Increasing the NaOH contents in the etching solution to 2% and 3% somehow provides similar etching rate increment profiles but the resultant surface roughness values are smaller than that of 1% NaOH. It is believed that at 1, 2 and 3% NaOH concentration, film surfaces experience similar etching reaction. Thus, film surface after by-product lift off should be the similar for those three etching compositions. Affinity of NaOH as etchant towards the by-product should be more pronounced than film surface due to the loose compaction and higher surface areas than the film surface itself. The 2 and 3% NaOH etching solution somehow provides more NaOH etchant which contributed to more dissolution of surface and by-product. This etching process contributes towards a smoother film surface. On the other hand, 1% NaOH suffers insufficient NaOH etchant where most of the NaOH ions have been consumed by dissolution of by-product leaving a rougher

surface which exhibits higher roughness than the ones produced from the 2 and 3% NaOH. Etching solution with 4 and 5% provides different etching pattern in which higher etching rate can be clearly observed. Due to higher etchant composition, it is easy to dictate that these compositions provide higher etching activities on film surface and by-product thus contributing to higher surface grazing on both surfaces.

Another interesting feature observed during the study is that the higher surface roughness values obtained for samples etched at a longer time in higher NaOH percentages of 4 and 5%. It is observed that the increment has achieved stagnant states of 3.15 to 3.17 nm for 5% NaOH and 3.13 to 3.16 nm for 4%. This condition indicates that etching process of dissolving of $VSiO_{3/2}$ into NaOH:ethanol solution has been significantly reduced. This could be explained by correlating the concentration of NaOH with etching time. The chemical reaction to dissolve the hybrid organic-inorganic matrix at the surface has been reduced due to formation of NaOH particles that occurs in higher concentration of NaOH allowed to react within a longer period of etching. The formation of NaOH particles is also known as recrystallization on film surface has blocked or retarded subsequent chemical reaction that should occur between film surfaces and NaOH ions. NaOH in particles or solid states is not active to promote dissolution process.

3.3. Influence on optical properties of film thickness

Effects of the wet etching process are further studied from the physical aspects in terms of optical film thickness. Based on the previous discussion, an etching solution with 2% NaOH composition has been selected to study the elongation of film thickness with etching process. Detection of film thicknesses were executed on the both irradiated and non-irradiated areas by using spectroscopic reflectometer via thickness mapping mode.

Initial film thickness before wet etching process has been set at around 1.0 µm and detection of thickness loss were monitored for every 3s. Fig. 6 showed reflectance spectra of thin film for before and after 10s etching process applied. Reduced on the number of maxima and minima on the spectra with wet etching indicating the loss of film thickness [18], however the maxima and minima for both spectra still pointed at similar imaginary line of upper and lower envelope suggested that both thin film condition having similar optical properties of refractive index, concluded that the wet etching process do not affected the refractive index of the subjected material. From Fig. 7, it is clearly observed that non-irradiated area exhibits a dramatic loss in film thickness within 7s in etching solution. Film thickness for that area has reduced from around 20 to 50 nm after 15s of etching process applied. In between 9 to 15s of etching, there is a steady state of thickness reduction. These observations indicated that etching reaction of dissolution of non-irradiated area has occurred vigorously within the early stage of etching process. The steady state of dissolution that was observed from 9 to 15s showed that previous reaction of dissolution on the surface has slowed down. This may due to the increase of the leached-out by-products in the etching solution that consumed NaOH ions. This condition reduces the number of NaOH ions that expected to react with the film surface. Longer etching time shows that etching activities was further reduced until the film's thickness reached around 20 to 50nm. The remaining layer is believed to form a strong adhesion with SOS (silica on silicon) of substrate surface.

Fig. 7 also indicates that irradiated areas also suffer from a thickness reduction of 7% from the initial film thickness. However, from the perspective of durability against etching ions without photoresist, the irradiated area still showed to be durable against massive alcohol alkaline etching solution.

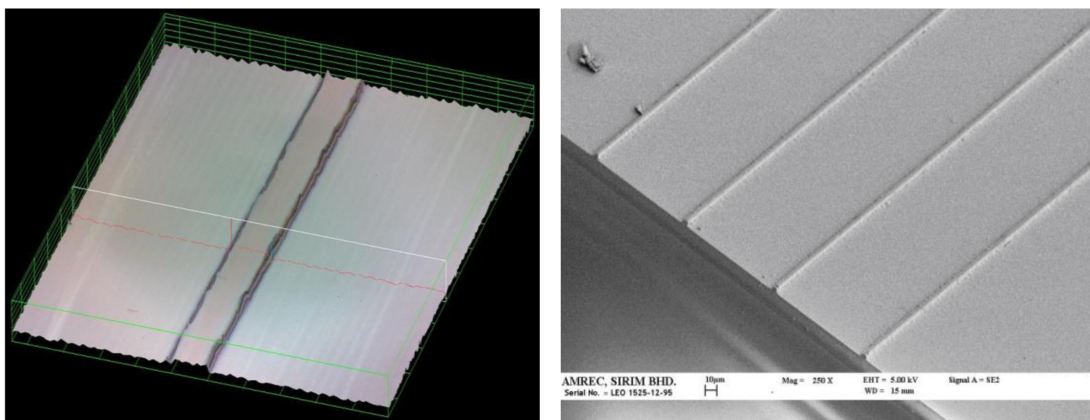

Fig. 1. Confocal and FESEM micrograph of the etched photosensitive thin film on substrate

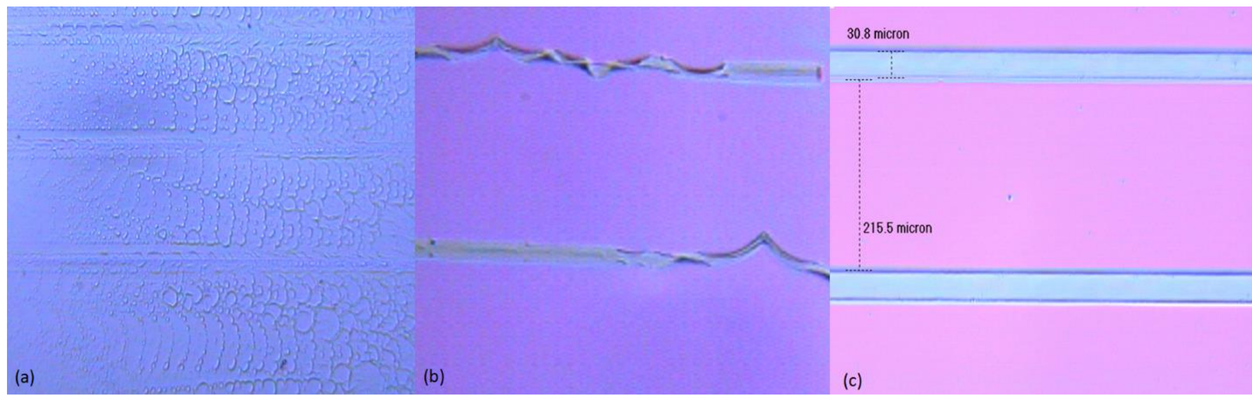

Fig. 2. Optical micrographs of waveguides pattern; (a) incomplete etching with etching time of less than 15s, (b) patterns lift-off from substrate after 30s, and (c) complete etching of non-irradiated areas between 15 to 30s

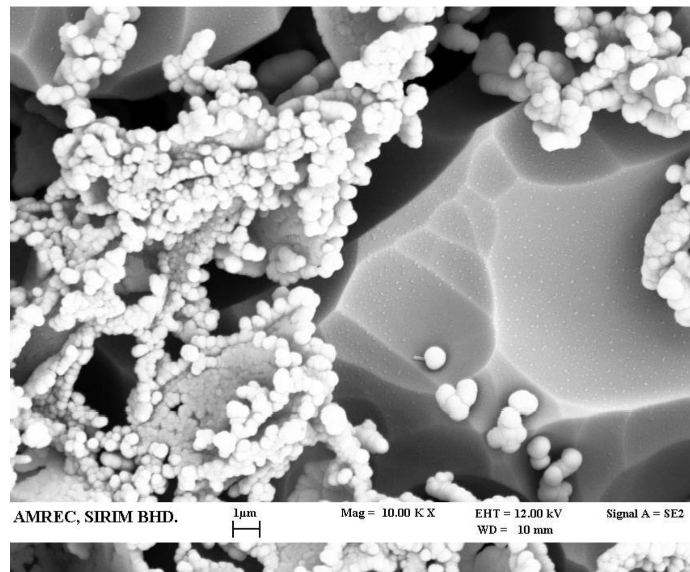

Fig. 3. FESEM micrograph showed the redeposition of NaOH on the etched areas

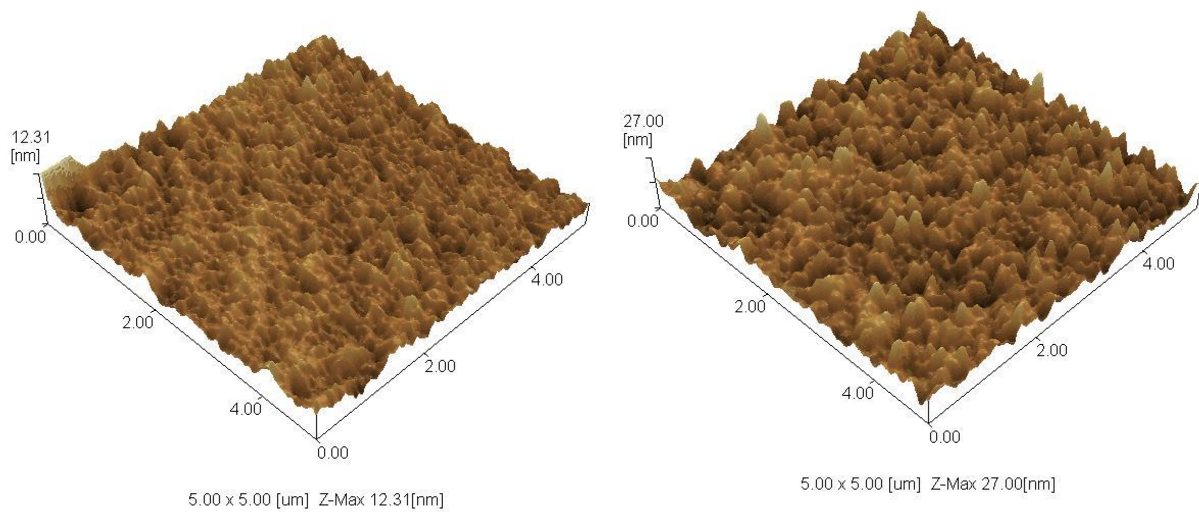

Fig. 4. Atomic force micrograph of etched vinyl-silsesquioxane thin film surface for (a) before and (b) after 30s etching

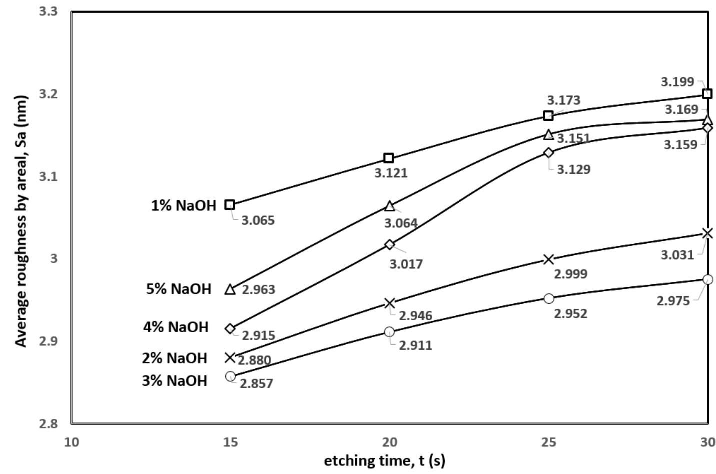

Fig. 5. Average areal roughness, Sa on irradiated areas of vinyl-silsesquioxane thin film with different etching time and NaOH composition

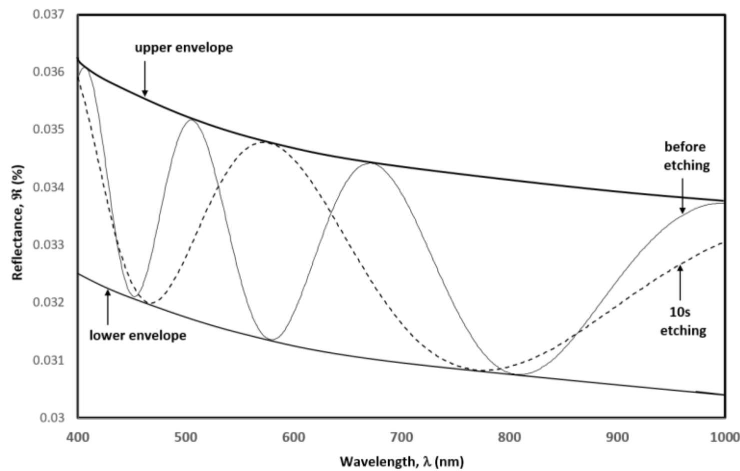

Fig. 6. Reflectance spectra on the vinyl-silsesquioxane thin film for before and after 10s wet etching

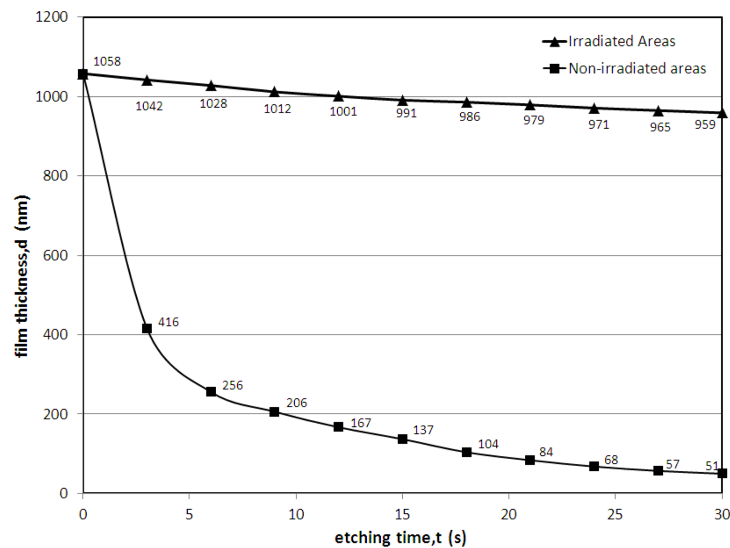

Fig. 7. Loss of film thickness for irradiated area and un-irradiated areas

4. Conclusions

In general, the results of the study revealed that UV irradiation induced structural changes of vinyl-silsesquioxane thin film by performing photo-addition polymerization of vinyl groups to form saturated crosslinking organic network. This induced structural changes improved the resistivity of film matrix towards alkaline alcohol etching solution. Controlling etching solution at below 2% at specific etching time of 15s by using shorter alkyl group alcohol governed

more definitive pattern transfer through UV-micro-patterning technique with average areal roughness, Sa within 2 to 3 nm.

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