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Silica Titania Optical Thick Film by Multi-spinning Sol-gel Process

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ABSTRACT

Sol-gel process has been used for producing high purity and homogenous optical thin films. A high quality, crack free optical thin film and low processing cost are key success factor for optical applications especially in planar waveguides technology. However, film cracks always occur in the silica and silicate base thin films as the thickness of thin film reached above 1m by multi-spinning sol-gel process. Proper handling and consistence conditions was studied using the silica-10% titania sol deposited on silicon wafer substrate. The dry gel silica-10% titania thin film was heat-treated at 680°C using Rapid Thermal Annealing (RTA) furnace. The Rapid Thermal Annealing (RTA) furnace was designed in-house by modifying tube furnace and the required heating rate was set manually. Under controlled deposition conditions in 10K clean room, crack free films ~2 micron thick have been successfully fabricated. However, lack of control in the deposition process can generate dust from excess sol-gel sol during spinning process and then contributes to point of stress in the thin film and cause formation of spider web crack pattern.

Keyword: Sol-gel process, silica-10% titania, thick layer and spider web crack pattern.

INTRODUCTION

Sol-gel process has been proven to produce high quality optical coating at low production cost and a practical approach in fabricating planar waveguide devices [Łukowiak *et al.* 2005]. Silica and silica-titania materials in sol-gel process have been widely research for use in optical applications with refractive indices ranging from 1.4 to 2.3 [McDonagh *et al.* 1996, Karthikeyan and Almeida 2000]. The high compatibility of sol-gel coating to produce silica and silica-titania thin film coated on different kind of substrate materials and the ability to tailor their refractive indices make them suitable for optical interconnection [Almeida and Vasconcelos 1997, Ballato *et al.,* 1997].

The fundamental reactions that take place during sol-gel process involved both hydrolysis and condensation reactions which can influence the properties of the final product. The process of hydrolysis reaction is more rapid and complex when catalyst was added in the process. The acid-catalyzed hydrolysis at equivalent catalyst concentration proceeds faster compared to base-catalyzed hydrolysis. It is normally preferred in sol-gel science to choose acid-catalyzed condition at pH2 to influence the hydrolysis rate of sol-gel process [Brinker and Scherer, 1990]. Introduction of titania into catalyzed silanol network during condensation process improved the gelling time [Enomoto *et al.,* 2002]. The sol tends to form linear molecules when gelling time is longer, thus increase cross-linking, formed stable region and reduced crack [Brinker and Scherer, 1990].

In sol-gel process, a series of spin-coating and annealing cycles were needed to build up micron-thick optical materials layers. Fardad *et al.* (1995) reported difficulty in achieving silica thin film thickness of more than 1 μm using spin-coating technique. The film deposition process on the substrate involved transformation of sol from gelling stage to glass stage with removal of majority solvent in the gel film. The sol viscosity conditions for coating process can influence the final thick film formed such as stress, higher shrinkage and shear [Brinker and Scherer, 1990]. The film experience intense stress under heat treatment during the densification process [Brinker and Scherer, 1990]. Non-uniform film thickness also contribute to form crack due to intrinsic stress especially after thermal treatment [Ahmad Makarimi *et al.* 2004].

This paper discusses the contributing factors on crack patterns formation for silica and silica-titania thin film materials by sol-gel process. Research is still going on to investigate the cause and how to minimise crack problems on thin film.

EXPERIMENTAL PROCEDURE

Silica thin films were prepared from Tetraethoxysilane (TEOS, 98% Fluka), Ethanol (EtOH, 98% Fluka) and Hydrocloride Acid {HCl (aq)} in molar ratio of 1: 6: 5. The solution was stirred at least 24 hours before it was diluted with ethanol and aged for 18 hours before the spin coating process. All sol solutions preparation was done in the glove box.

Silica-titania thin films were prepared by introducing Titanium Butoxide (TtBu) precursor into the silica sol prepared in the same manner as above procedure. The titania sol was first prepared from Acetylacetone (Acac; 99% Fluka) and Titanium Butoxide (TtBu; 99% Across) in molar ratio 1:4 (Acac: TtBu). Before spin coating process, the mixed silica-titania sols were stirred for 24 hours before diluting with ethanol and aged for another 18 hours.

Both silica and silica-titania clear sol solutions obtained were filtered using a 0.20μm filter and served as coating solution. The coating was carried out by spin coating process on glass substrate with a speed of 3000rpm for 30s in 10K cleanroom with controlled temperature and relative humidity at 25°C and 30%-40%RH respectively. Consolidation of the deposited layer was done using Rapid Thermal Annealing (RTA) a 680°C. The deposited layers for all samples were span four times before each consolidation process was done. Multiples spinning were used to build-up thick film of optical quality.

Then, characterization of silica and silica-titania films morphology of optical thin films was obtained using reflected light microscope and LEOS 1525 Scanning Electron Microscope (SEM).

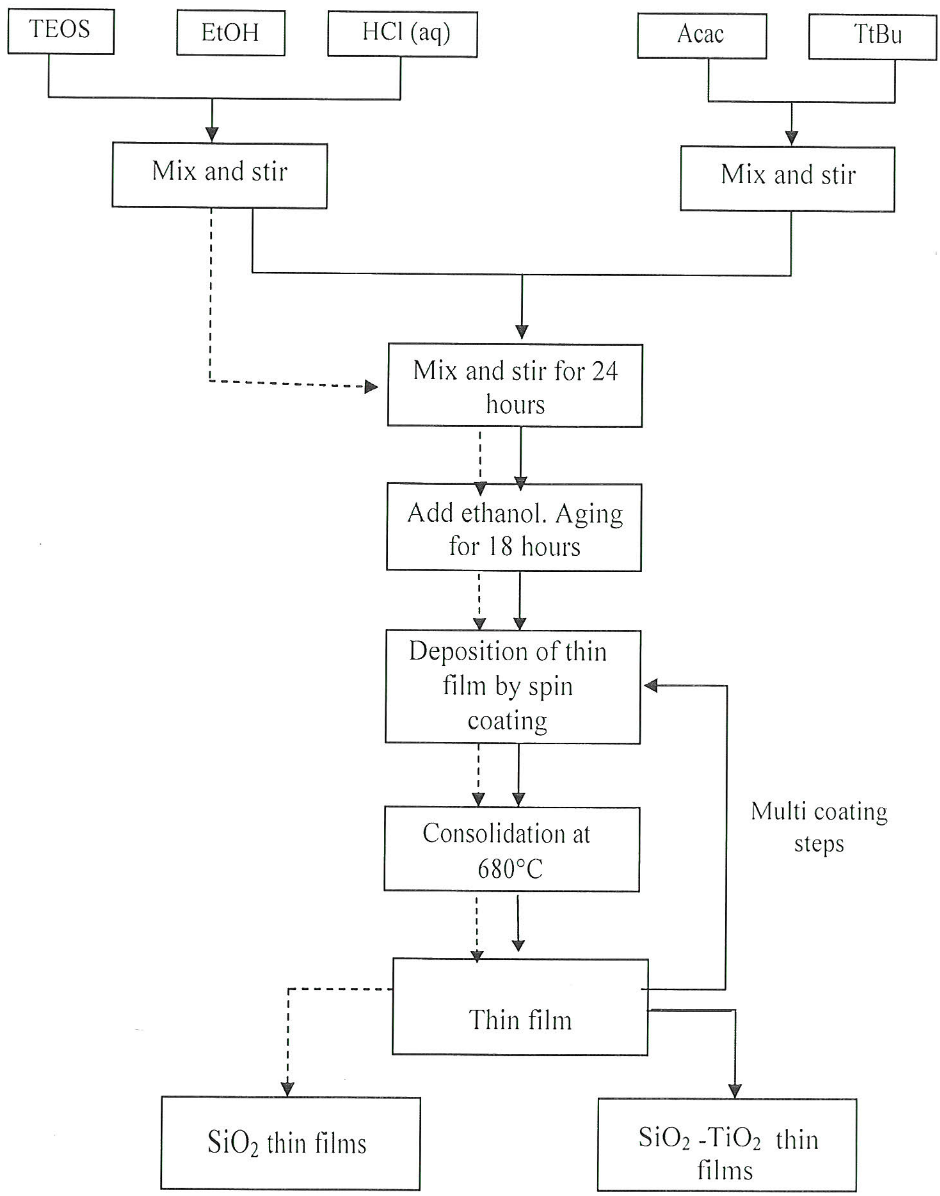

Figure 1. Preparation route for SiO2 thin film (--------) and SiO2 – TiO2 thin film (solid line) by sol-gel process.

RESULTS AND DISCUSSION

Sol-gel spin coating technique involved four stages to form dry gel thin film: deposition, spin-up, spin-off and evaporation [Brinker and Scherer, 1990]. At the evaporation stage, the film formation steps comprise of the following steps:

1. Dry gel thin film where the sample was dried at room temperature.
2. Further evaporation with thermal heating at $680^{\circ}C$ for two minute.
3. Multilayer deposition to build up thick layer for optical purposes.

The crack film phenomenon in film samples is often observed at then third steps during building up film thickness via sol-gel process. All observations were done by comparing results obtained from SiO2 thin film and SiO2 - TiO2 thin film.

Step 1: Dry Gel Thin Film.

For the silica thin film preparation, the silica sol was span twice on the silicon wafer at room temperature. The first layer was observed to be homogeneous and crack free. However, the subsequent layer evolved patterns of multiple cracks similar to mud-S crack pattern which was introduced in worked [Liang *et al.*, 2003]. Figure 2 shown multiple crack surface morphology of second layer deposited using silica sol sol-gel process. This maybe explained by the water and ethanol condensation dominates the sol-gel reaction and also solvent evaporation happen between 1^{st} and 2^{nd} film layer. The process of building up silica thick film was discontinued at this stage.

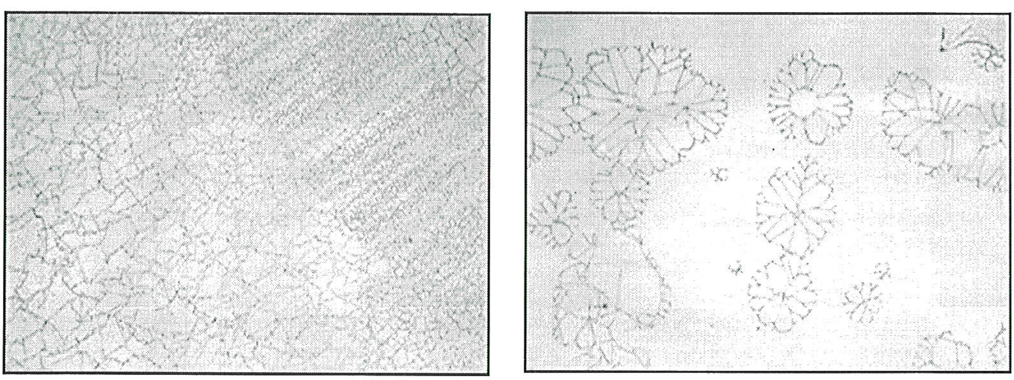

Figure 2. Optical microscope image of dry silica gel thin films after two times deposition process on si-wafer at room temperature. Multicrack film was observed similar to mud-crack pattern.

Crack free thin film for silica based thin film can be fabricated by controlling the sol-gel spin coating environment with 42%-50% humidity and 20°C-30°C temperature [Ahmad Makarimi *et al.,* 2004]. To further improved the percentage of crack free thin film coated on si-wafer at room temperature by multi-spinning process, 10% of titania sol was added into silica sol. Figure 3, shows crack free silica-titania thin film (prepared from 90% silica + 10% titania sol solutions) deposited on Si-wafer by depositing 4 times span thin layer before the layered films were consolidated at 680^{Z}C under Rapid Thermal Annealing process (RTA). The crack free silica-titania based film thickness of more than 1µm using spin-coating technique was able to achieve, which is about 1.38µm thickness.

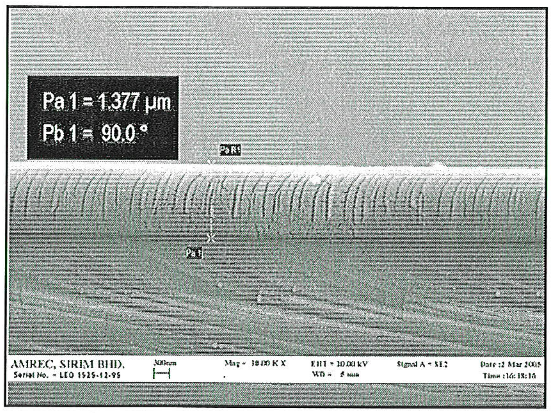

Figure 3. SEM micrograph of crack free thin film silica-titania (prepared from 10% titania + 90% silica sol) at 680°C with thickness of 1.38µm.

Step 2: Multi-deposition and Multi Rapid Thermal Annealing (RTA) at 680°c for Building Up Thicker Layer

It was observed that most of silica based thin films have shown cracks above 1µm. Figure 4, shows the SEM micrograph of silica based after undergone 10 times rapid thermal annealing heat treatment. At film thickness 1.77µm, the film cracked and the subsequent deposition for building up the thickness layer was not able to proceed. Figure 5 shows side view of peel of layer of silica based thicker films from the si-wafer substrate.

For silica-titania based sample we are able to fabricate crack free thin film and achieved thickness up to more than 2µm. In running the experiment for multiple deposition care need to be taken on the issues of silica flakes from dried sol and dust which have been known to deteriorate the film quality. Figure 6, shows morphology of crack free silica-titania based sample prepared with multi-layer deposition and 17 times RTA at 680°C, having thickness nearly 3µm.

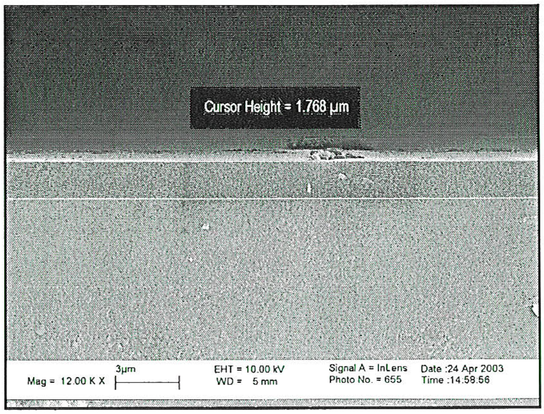

Figure 4. SEM micrograph of silica based crack film with 10 times RTA at 680°C. Further deposition for building up thicker layer was not able to proceed above 1.77µm thickness.

The additional of TiO2 to a SiO2 network occurs by the continuous substitution of tetrahedrally coordinated Ti4+ for Si4+ and form silica-titania structure [Brinker and Scherer, 1990]. Addition of titania improved crack from occurring in the thin film for thickness above 1µm under maximum precaution of dust, humidity and temperature control during the spin coating process. It seem that tetrahedrally coodinated Ti4+ will reduce structural stress from Si4+ after transform from sol form to gel form in thin film.

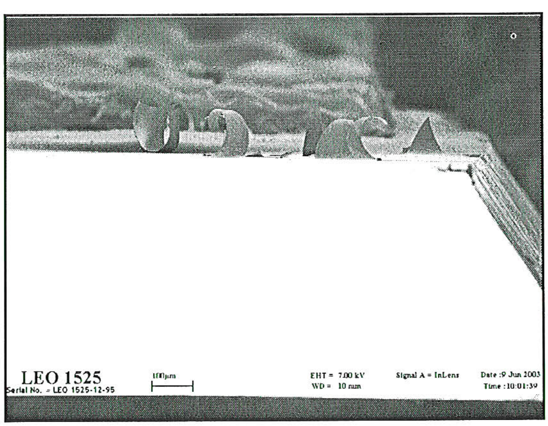

Figure 5. SEM micrograph of side view silica based crack film. The layer was peeled off from the Si-wafer substrate.

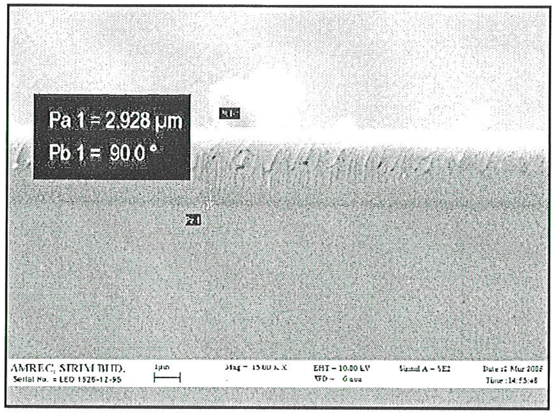

Figure 6. SEM micrograph of crack free thick film silica-titania (prepared from 10% titania + 90% silica sol) with 17 times RTA process at 680°C. The film thickness is 2.93µm.

Dust is a major issue in the process of spin sol-gel process [Mat Tamizi *et al.* 2003]. Dust or particles can be trapped between the layers during spinning process. The nano and micro hair size crack film was induced from the first layer and then spread out to the upper layer in the process of building thick film. Heat treatment applied on thicker sample also causing high stress on the film. Figure 7(a) and 7(b) show spider web liked crack pattern forming from thicker and thin straight crack advancing toward each other at the nucleation centre.

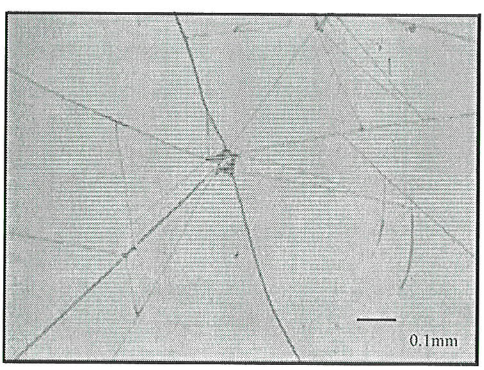

Figure 7(a). Optical microscope image of silica titania thin film (prepared from 10% image of silica-titania thicker film exhibited titania + 90% silica sol) showing spider web crack pattern.

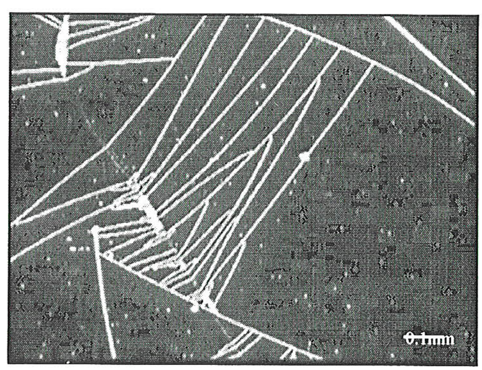

Figure 7(b). Optical microscope dark field image of silica-titania thicker film exhibited crack advancng toward each other forming spider web crack pattern. (5x mag.).

CONCLUSION

The crack film phenomenon in film samples are often observed during building up film thickness via the sol-gel process. Dust problem need to be controlled during the spin coating process. The film also experience intense stress under rapid thermal annealing heat treatment during the densification process. The introduction of titania into the silica structure improved the percentage of cracked film. Mud-crack pattern was observed for the silica based film while spider web liked crack pattern was observed for the silica titania based film.

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