A Review of Wet Chemical Etching of Glasses in Hydrofluoric Acid based Solution for Thin Film Silicon Solar Cell Application

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ABSTRACT: High efficiency thin film solar cells require an absorber layer with high absorption and low defect, a transparent conductive oxide (TCO) film with high transmittance of over 80% and a high conductivity. Furthermore, light can be captured through the glass substrate and sent to the light absorbing layer to improve the efficiency. In this paper, morphology formation on the surface of glass substrate was investigated by using HF, mainly classified as random etching and periodic etching. We discussed about the etch mechanism, etch rate and hard mask materials, and periodic light trapping structure.

Key words: Light trapping, Wet etching, Chemical, Hydrofluoric acid, Thin film, Solar cell

1. Introduction

Glasses, due to their unique properties, are widely used in the optical devices, MEMS devices, and solar cells. The optical transparent and the ability to withstand much light scattering influences can be considered as the most remarkable properties in this respect. Glass is a combination of the relative ease with which the material can give the desired shape due to its unique the light trapping properties of the solar cell.

The thin film silicon solar cell is a great potential as photovoltaic devices. The production on a large scale in a fully automated manner allows glass substrate and low material usage, low cost per watt is better than crystalline Si solar cells.1,2) In thin film silicon solar cells, hydrogenated amorphous silicon (a-Si:H) or microcrystalline silicon (μc-Si:H) used as an absorption layer. To have an effectively light absorption to the solar cell, light management in the textured surface is necessary for the high-efficiency solar cell. Surface texturing can result in enhanced scattering from transmitted light and then low reflection on the surface of the incoming light.3)

Textured surface increases the optical path length, which is improved the photocurrent and quantum efficiency as well. To make the surface morphology of the light trapping, it obtained by etching process like wet chemical, dry and direct pattern.4-6) Textured surface allowed more light scattering and low reflection at rough internal interfaces, leading to more efficient light trapping and subsequent increase of light absorption in the solar cell. Textured surface regarding light trapping carried out on the transparent conductive oxide layer (TCO) of thin film silicon solar cells. Chemical etched AZO films shows better light trapping properties, it is only efficient at shorter wavelengths, but with relatively decreases at longer wavelengths. It must be obtained to reduce the loss for better light scattering and internal reflection. It can be readily dissolved by hydrofluoric acid or other HF containing aqueous solutions at room temperature.7) Controlled dissolution in HF-based etchants can be applied to remove material using related glass application. Wet chemical etching of glasses in aqueous HF solutions is a subject that has studied for many years. Scheele et al. reported about the discovery of HF in 17718) and then is being studied more extensively, due to the solar cell application for the light trapping as the substrate.

For achievement of better light trapping using etching technique, it considered for scattering effect having a small-sized structure in the short wavelength and large sized structure in the long wavelength region, respectively. Recently, there are several reports related to the etching by random, periodic using photolithography pattern for light trapping; most research is rarely systematic study for the substrate of thin film silicon solar cells. In this study, the reaction mechanism, etch rate as well as the surface morphology reviewed, and the effect of the glass types,
etchant types and hard mask layers discussed. Finally, application and conclusion described.

2. The etch mechanism, etch rate, and glass types regarding random etching of glass by wet chemical

2.1 The etching reaction: HF, HF/HCl, and HF/H$_2$SO$_4$ (mechanism)

For the etching of glasses, only hydrofluoric acid or other HF containing aqueous solutions used. The chemical reaction regarded as the following:

$$\text{SiO}_2 + 6\text{HF} \rightarrow 2\text{H}_2\text{O} + \text{H}_2\text{SiF}_6$$

This equation is a simplification of the reactions during the heterogeneous SiO$_2$ dissolution as shown in Fig. 1 (a). HF is made up of the corrosive hydrogen ion (H$^+$) and the toxic fluoride (F$^-$), thereby acting in two ways (see picture above). The acid corrodes the glass surface and thus allows the toxic fluoride ion to penetrate the glass. Once in the glass, the fluoride ion binds themselves among others calcium and thus disturb the other chemical components of the glass$^{10,11}$. Glassy SiO$_2$ consists of tetragonal SiO$_4$ units connected at all four corners to four other SiO$_4$ units by covalent siloxane bonds$^{12}$. It is necessary to break these bridging oxygen bonds to break down the network and release silicon from the glass. HF, dissolved in water, is a weak acid and its solutions containing, H$^+$, F$^-$ and HF$_2^-$ ions and un-dissociated HF molecules$^{13}$. The dissolution of glassy SiO$_2$ is a heterogeneous reaction, which makes it difficult to study the mechanism governing the dissolution process. However, the breaking of all the chemical bonds, which results in eq. (1), will require several reaction steps. At first, glass reacts with HF forming silicon tetra-fluoride and water and SiF$_4$ reacts with HF to form H$_2$SiF$_6$, which is not soluble in HF solutions.

By adding to buffer acid agent such as HCl, HNO$_3$, H$_3$PO$_4$ and H$_2$SO$_4$ to HF solution, the concentration of the more reactive HF ion in the etchant is lowered, following equation (2) and (3)$^{14}$.

$$K_1 = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$

$$K_2 = \frac{[\text{HF}][\text{F}^-]}{[\text{HF}_2^-]}$$

$$K_1 = 6.74 \times 10^{-4} \text{ mol/l}, \quad K_2 = 0.26 \text{ mol/l}$$

![Diagram of glass etch mechanism based on (a) HF, and (b) HF/H$_2$SO$_4$](image-url)
Only in etchants containing both HF and concentrated H$_2$SO$_4$ were the etch rates higher than for HF/HCl or HF/HNO$_3$ etchants, an effect which described to the formation of active fluorine-containing HSO$_3$F acid. For further detailed information, the role of buffer acid etchant from HCl to H$_2$SO$_4$ presented as shown in Table 1.

A higher HF concentration generates the by-product H$_2$SiF$_6$ in the first reaction, and then the regeneration of the HF occurs after the second reaction with the H$_2$SO$_4$ during the etching process. The HF concentration continually maintained along with the sulfuric-acid changes, and this then continues with the increasing of the activation energy. The addition of H$_2$SO$_4$ is, therefore, effective for the increasing of the etch rate and the surface roughness. The HF-H$_2$SO$_4$ etching systems, an effect that ascribed to the formation of the strong fluorine-containing HSO$_3$F acid$^{15}$. From the etching of the surface, these surfaces are less smooth than the mechanically polished ones, meaning that it is possible to transform ground surfaces into optically transparent surfaces as shown in Fig. 1 (b).

As mentioned above, the etch mechanism of HCl to HF is slightly different. Initially, the HF solution etches the glass and insoluble byproduct deposited on top of the glass surface. As the time goes on progressed, the size of insoluble byproducts becomes larger and accumulates to interfere with etching on the glass. However, HCl (other oxide series) releases impurities in HF-HCl mixed solutions [ref 16, JNN 2016 Park et al.]. Thus, it can be seen that the similar shape as the crater surface appears as shown in Fig. 2 (b).

The etch rate of agitation of the solution is related to the adsorption or chemisorption on the siloxane bonds at the glass surface dominating the dissolution process. The etching mechanism, in particular, the role of the various fluorine-containing species, has studied in more detailed by many researchers for the etching rate.$^{8,15,17-19}$ Fluorine absorption complexes have observed at hydrated SiO$_2$ surfaces in gaseous HF. It changed into a surface group such Si-F or Si-O-SiF$_3$. The absorption of HF and HF$_2^-$ increases the electronic density on the bridging oxygen more.

![Fig. 2. A SEM images of etched surface as a function of etching solution (a) HF, (b) HF+HCl, and (c) HF+H$_2$SO$_4$.](image)

Table 1. The role of buffer acid etchant

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<th>Etchant</th>
<th>The role of buffer acid etchant</th>
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| HF      | 1) Involved in the etch rate of glass: fluorine containing species  
2) Insoluble products generation as masking layers on glass substrate during etching: textured surface becomes rough and non-uniformities |
| HCl     | 1) Significantly reduced roughness of side wall  
: preventing the formation of alkaline earth fluorides with low solubility on the surface, the etching rate of HF+HCl etchant was not sufficiently stable & can transform insoluble products to become soluble. |
| HNO$_3$ | 1) Faster longitudinal etching rate  
: Due to the strong oxidability of HNO$_3$ which facilitates the reaction between HF and glass |
| H$_3$PO$_4$ | Lower etching rate |
| H$_2$SO$_4$ | 1) HF+H$_2$SO$_4$ etchants: the formation of the strong fluorine-containing HSO$_3$F acid. By etching the surface, these surfaces are less smooth than mechanically polished ones; it is possible to transform ground surfaces into optically transparent surfaces. |
basic, so more $H^+$ ions are adsorbed, which leads to more siloxane bonds being broken per time units, for example a kind of catalytic effect. Determination of the etching rate is then the destruction of the siloxane bond by the plus action of the adsorbed species.

The catalytic action of $H^+$ ions on breaking siloxane bonds also occurs in the dissolution of glasses in acidic and weakly alkaline solution\(^{18}\). Methods for the decision of the etch rate of glasses are several ways as follows: The weight loss of dispersed powders, partially masking the surface of a glass body, e.g. a disk, by photoresist or wax. The etch rate for the glass is measured by monitoring the depth of the recessed etched region after etching of glass. It is slightly affected by agitation of the etchant from the rotation, stirring or ultrasonic.\(^{19}\)

2.2 The surface morphology, etch rate, and the glass types for etching of glass

Glass etching process not only removes surface products, but it also changed the surface morphology of the glass depending on the etching solution. When polished, the surface has slightly etched the surface roughens and verge-like structures. The experiment carried out to confirm the light trapping structure by varying the type of glass as shown in Fig. 2. Here, HF solution of $\sim 50\%$ was used as the glass etch solution and etch time is 10 min. The Corning Eagle XG glass showed a smooth surface, while super-white glass had a severely rough surface and observed the texturing size of the tens to hundreds of $\mu$m. Although the same HF solution used, it showed the surface properties depending on the type of glass and related to the chemical composition of the glass.

We investigated three kinds of glasses such as Corning Eagle XG, soda lime, super white to understand for the etching of glass. This table shows the chemical composition, optical properties and thermal resistance of glass as a representative three kinds of glasses. Silicon dioxide ($SiO_2$) constitute more than fifty percent of total glass composition as shown in Table 1 and it included in calcium oxide ($CaO$) or sodium dioxide ($Na_2O$) or aluminum oxide ($Al_2O_3$) according to the kinds of glasses\(^{20}\). In the case of optical properties, the transmittance is around 92% at the wavelength of 500 nm and around 8% for the reflectance. Corning Eagle XG glass is superior to the different things in quality for the thermal resistance of more 600°C. However, Corning Eagle XG glass cost per units was more expensive than other glass because of less dopant component in the glass.

It shows that this formation is related to the presence of some products when etching of glass. Etched shape related size or depth is presenting after etching to large cracks formation by the products. Fig. 3 shows that the growth of product increased and this surface morphology is gradually changed into a verge as the etching process. This process indicates a size-up of fluorine

\(Fig.\ 3.\ Top\ view\ images\ of\ product\ size\ formed\ on\ a\ glass\ substrate\ by\ the\ etching\ treatment\ in,\ (a)\ 30\ min,\ (b)\ 60\ min\ and\ (c)\ 90\ min,\ respectively\)
products on the glass surface and a diffusion of fluorine species, which is related to the etching rate. Therefore, we have a conclusion that fluorine products play a crucial role in the macrocrack formation with random-etching without masking layers.

Based on the facts mentioned above, it affects the glass texturing depending on the type of glass, composition ratio of the etching solution, temperature, and agitation. Fig. 4 shows that etch rates investigated according to various glass types, and HF 25% (volume ratio of DI:HF = 1:1) was fixed. The graph shows that the etch rate of the SiO$_2$-based glass (Fused natural silica) substrate having a low impurity content lowered even though it is the same solution. It contained less impurities of the glass substrate, which reported in previous research groups.$^{21,22}$

3. Investigation of periodic textured glass morphology

3.1 Glass etching and hard mask layer types

So far, we have briefly discussed the random etching surface using wet chemical etchant. To solve this problem as per the previous subchapter, we are going to talk about wet etching with periodical pattern mask. It is a well-constructed periodic etched shape as referred in$^{23}$. The Periodically patterned shape has various light trapping structures such as high aspect ratio, square type, honeycomb, hemisphere as shown in Fig. 7. We should take into consideration such as masking materials, adhesion between substrate and masking layers, masking layer height, and size, spacing, and shape of the pattern to have an optimized light trapping structure. It is related to make the light trapping structure on a glass substrate having mask pattern and etching solution.

Fig. 5 presents the glass etching step (before etching ~ etch-4) for isotropic etching. This is possible for making a high aspect ratio structure according to specific etching step. It is crucial factor such as the concentration, time, and solution ratio of the etching for high aspect ratio structure, but they also depend on the characteristics of the mask layer material. We investigated regarding the effect on the hard mask material as shown in Fig. 6 to improve the light trapping structure with the periodic pattern.$^{17}$ The photoresist (PR) is used as the most commonly used masking material in wet chemical etching. When the concentration of HF increases or deeper etch performed, it is
easy to be penetrated by HF acid between the glass and PR. Metal is widely used to serve as the masking layer. For the Comparison to a photoresist, the HF molecules get absorbed inside the inherent pinholes and cause the enhanced defects on the glass surface. The Al–glass adhesion was still too weak to prevent the lateral HF penetration for long-time etch. The silicon-based thin film is another well-known inert material to HF, it shows excellent adhesion with the glass substrate, and more importantly, the surface of the silicon-based material is hydrophobic which highly prevents the formation of surface pinholes and notching effect during the HF etch. This property implies that this masking material could be a good candidate for deeply fused silica etches.

One of the process steps is checking for hardening the photoresist (PR)/HMDS solution, and the other is maintaining the etchant temperature during the etching. Masking layers are not only PR/HMDS but also different materials such as hydrogenated intrinsic amorphous silicon layer (i-a-Si:H) or silicon nitride (SiNₓ) by PECVD, metal mask like Al or Cr by the thermal evaporator (or sputtering), a thermal oxide (SiOₓ). All of masking materials excepting for PR/HMDS layers need to remove Metal or (SiNₓ or i-a-Si: H) with RIE or wet etching right after hard baking. However, and PR/sub-layers on the glass have excellent etching characteristics like a high aspect ratio, isotropic etching, selectivity and fast etching without a new process (RIE process).

3.2 Wet etching parameters and light trapping structure

Fig. 8 shows the light trapping structure for Etch-3 at different mask pattern from (2×2) to (15×2), which are based on wet etching.

It consists of 2 types such as randomly textured surface without a pattern and periodically textured surface with the pattern. The textured surface used to be captured the light are based on the crystalline silicon (c-Si) solar cell as a substrate and thin film silicon solar cell as superstrate or substrate as well. In
the mask pattern, the spacing is fixed at 2 μm, and the size gradually increases. As the size increases, the etching height gradually increases. The increase in the etching height serves to capture the incident light and increase the light scattering effect. In this way, the haze ratio can be determined using a haze meter or integral sphere to determine the light scattering effect.

The haze ratio value according to the mask pattern change is shown in Fig. 8. As shown in the figure, the mask pattern of (10×2) or more maintained an average haze ratio of 50% or more to the long wavelength region. However, using the same structure as in the figure, the haze ratio is more than 60%. This requires careful examination of various parameters such as height, spacing, and shape of the structure.

4. Application and Conclusion

Based on HF containing a solution, we used as a device application such as MEMS, biotechnology and photovoltaic based on HF glass etching to better the life. In this section, we have discussed the brief applications and concluded in our work. Glass etching process regarding the purpose of thin film solar cell applied satisfactorily when the textured glass surface is free from contaminants. The etching key point necessary to clean a glass surface depends strongly on the etching solution and concentration for the light trapping structure. This changed by alternating short time etching of glass substrate with HF/H2SO4 without etching mask. Transforming smooth surface into optical light trapping morphology is possible.

Although the reaction mechanism did not understood at this moment, we are available for the use of an industry if having satisfactory experiment results. HF solutions considered dangerous together with insoluble products. Therefore, it is of great importance to reduce the quality of the etchants used during the work and to develop methods to apply for the solar cell devices. For this work, it is replaced by dry etching on behalf of the wet etching to reduce the insoluble products. However, strong points of wet etching process are still better than that of dry etching because of a simple process, cost efficient and well-controlled the surface structures. Therefore, we will be interesting to see how the wet etching glass will be resolved.

Acknowledgment

This work was supported by the ‘New & Renewable Energy Core Technology Program’ of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea (No. 20153010012090).

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