Surface Energy Change of Si(100) Wafer by Exposing to Air

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By contact angle method, surface energy of Si(100) wafer is measured with lapse of time in ambient condition. The polar component \( \gamma_s^p \) of surface energy increases drastically but the dispersion component \( \gamma_s^d \) decreases. Surface energy \( \gamma = \gamma_s^d + \gamma_s^p \) gradually decreases. The surface energy change is mainly reflected with native oxide growth on the Si substrate. The polar and dispersion component of resist film corresponds mostly to those of surface energy of Si(100) after 10h exposing time to air. The spin coating condition can be designed effectively base on the surface energy model.

Keywords: native oxide, surface energy, dispersion component, polar component

1. Introduction

In ambient condition, a native oxide layer about 2nm thickness is formed on Si(100) surface. A HF aqueous treatment is one well-known process in order to remove native oxide layer formed on Si single crystal surface. In this regard, surface energy is sensitive to surface slight change of solid material.[1,2]

Particularly, wetting control of resist liquid becomes important in order to achieve uniform resist coating. In this study, surface energy change of Si(100) wafer after HF treatment is investigated by contact angle method. The possibility of surface energy matching of Si substrate with that of resist films is discussed.

2. Surface energy measurement

A Si(100) wafer was cleaned in organic solvents and it was dipped in hydrofluoric (HF) 5% solution in order to remove a native oxide. Then, the sample was rinsed in DI-water. Surface energy of Si(100) wafer surface was measured with the sessile drop method. The test liquids ware DI-water, diiodomethane and ethylene glycol. The test liquids were dropped onto the sample surfaces. Usually, surface energy \( \gamma_s \) of a solid surface is expressed as a sum of dispersion component \( \gamma_s^d \) and polar component \( \gamma_s^p \) as follows.[1,2]

\[
\gamma_s = \gamma_s^d + \gamma_s^p
\]

![Graph showing surface energy change of Si(100) wafer after exposing to air.](image)

Fig.1. Surface energy change of Si(100) wafer after exposing to air.

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Figure 1 shows the dependency of the surface energy on the exposure time to air. The polar component \( \gamma_s^p \) of surface energy increases drastically but the dispersion component \( \gamma_s^d \) decreases. Consequently, the surface energy \( \gamma = \gamma_s^d + \gamma_s^p \) of the Si wafer gradually decreases. The surface energy change is mainly reflected with native oxide growth on the Si substrate. It is well known that the Si(100) wafer surface is terminated with hydrogen termination group by HF treatment. Therefore, the polar component change is contributed with number density of hydrogen bonding on the Si substrate surface. Generally, native oxide growth reaches equilibrium for two days in ambient condition. The increased polar component can be considered as the hydrogen termination group on Si surface is replaced gradually with the Si-O bonding.

Figure 2 shows the component map of the surface energy of Si substrate. It is clearly observed that the polar and dispersion components of resist film correspond mostly to those of surface energy of Si(100) after 10h exposing time to air.

In general, the spin coating condition can be designed effectively based on the surface energy model.[1] The matching of surface energy components between two surfaces indicates higher wetting characteristic which is useful to design smooth resist coating on a substrate. The thickness uniformity of resist film can be control by adjusting the storage time of Si wafer to ambient condition.

The amount of surface energy at each exposing time is summarized in Table 1.

<table>
<thead>
<tr>
<th>Test liquids</th>
<th>( \gamma_s^d ) (mJ/m²)</th>
<th>( \gamma_s^p ) (mJ/m²)</th>
<th>( \gamma ) (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td>21.8</td>
<td>51.0</td>
<td>72.8</td>
</tr>
<tr>
<td>Diiodemethane</td>
<td>48.3</td>
<td>2.50</td>
<td>50.8</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>29.4</td>
<td>18.3</td>
<td>47.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Exposure time to the atmosphere</th>
<th>( \gamma_s^d )</th>
<th>( \gamma_s^p )</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 min</td>
<td>46.4</td>
<td>0.96</td>
<td>47.4</td>
</tr>
<tr>
<td>38 min</td>
<td>38.1</td>
<td>6.14</td>
<td>44.2</td>
</tr>
<tr>
<td>60 min</td>
<td>44.6</td>
<td>1.73</td>
<td>46.3</td>
</tr>
<tr>
<td>2 hour</td>
<td>42.7</td>
<td>3.29</td>
<td>45.9</td>
</tr>
<tr>
<td>3 hour</td>
<td>32.0</td>
<td>9.82</td>
<td>41.8</td>
</tr>
<tr>
<td>4 hour</td>
<td>40.5</td>
<td>3.10</td>
<td>43.6</td>
</tr>
<tr>
<td>6 hour</td>
<td>41.1</td>
<td>3.12</td>
<td>44.2</td>
</tr>
<tr>
<td>12 hour</td>
<td>36.0</td>
<td>5.91</td>
<td>41.9</td>
</tr>
<tr>
<td>1 day</td>
<td>33.6</td>
<td>8.68</td>
<td>42.2</td>
</tr>
<tr>
<td>3 days</td>
<td>28.1</td>
<td>15.2</td>
<td>43.3</td>
</tr>
<tr>
<td>7 days</td>
<td>35.4</td>
<td>6.42</td>
<td>41.8</td>
</tr>
<tr>
<td>14 days</td>
<td>26.6</td>
<td>22.7</td>
<td>49.3</td>
</tr>
</tbody>
</table>

Si substrate (cleaned) 25.8 25.8 51.6
TMAH developer 30.7 49.0 79.7
Photoresist-1 31.7 9.67 41.4
Photoresist-2 36.2 7.34 43.5

3. Conclusion

The surface energy of Si(100) wafer is measured with lapse of time in ambient condition. The spin coating condition can be designed effectively.

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References