

## In-situ Monitoring of Surface Process by Photo-emitted Electron in Photo-processing Systems

H. Itoh, M. Iwasaki, K. Tsukamoto and Y. Akasaka

LSI R&D Lab., Mitsubishi Electric Corp.

4-1, Mizuhara, Itami, Hyogo 664, Japan

Photoemission from the Si surface adsorbing the reactant gas was used as a probe for in-situ monitoring of the surface chemical process or condition. This method has an advantage that no evacuation or interruption of reaction is needed during measurement, thereby resulting in the observation of surface under the condition that the actual chemical reaction proceeds. Using this monitoring method, the type of surface state generated by the chemisorption of reactant gas was examined;  $\text{NH}_3$ ,  $\text{SiH}_4$  and  $\text{Si}_2\text{H}_6$  generate the surface state of donor type, while  $\text{HCl}$  acceptor type.

### 1. Introduction

There has been a view that charged particles do not exist in the photo-processing systems since no discharge of reactant gas is needed. However, quite a bit of electrons

are occasionally observed even in the photo-processing systems due to the photoemission. [1]

A feature of photoemission in the reactant gas is a considerable change of emissivity with the change of reactant gas or sample preparation procedure. A possible reason for this behavior of photoemission is a change of work function associated with the surface band bending as depicted in Fig. 1.

Since the surface band bending is caused or affected by the charge transfer through the surface states generated by the chemical adsorption of ambient gas or by the surface contamination, photo-emitted electron can be used as an in-situ diagnostic probe for surface process or surface condition. In particular, sensitive monitoring can be expected in the Si process because the typical value of the work function of Si is  $\sim 5$  eV and is close to the photon energy used in the UV photo-processing systems.

In this paper, some results of in-situ monitoring of surface chemical process using photoemission from the Si surface will be shown.

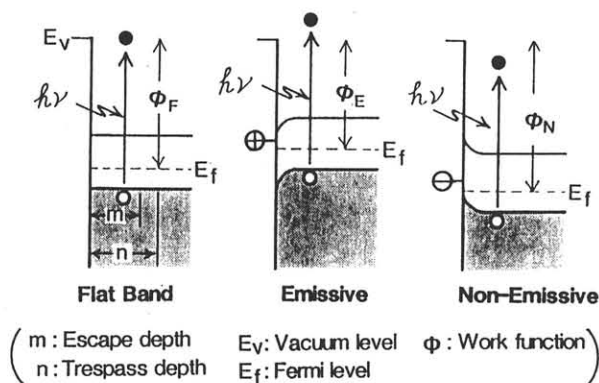


Fig. 1 Apparent change of work function accompanied with the chemisorption of ambient gas

### 2. Experimentals

Photoemission from the Si surface adsorbing the reactant gas was measured using an apparatus shown in Fig. 2. Available UV photons for photo-emission were of wavelengths of 185 nm and 254 nm from the low pressure Hg lamp. Photo-emitted electrons were collected by a DC-biased mesh electrode located at a distance of 3 cm from the sub-

strate surface. To avoid an influence of photoemission from the reactor wall, both the substrate and the mesh electrode including the external power supply circuit were electrically isolated from the ground level.

Further, applied electric field was kept as low as possible to avoid the undesirable collisional ionization in vapor phase.

Surface reaction could be excited not only photochemically but thermally and/or thermo-photochemically by radiantly heating the substrate up to  $\sim 700^{\circ}\text{C}$ . (100) oriented P-

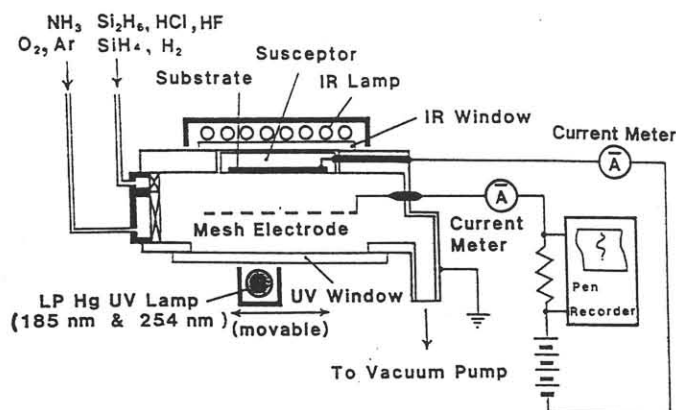


Fig. 2 Schematic diagram of apparatus

type Si wafers of 6 inch diam. were employed as substrates having line & space patterns of  $7500 \text{ \AA}$   $\text{SiO}_2$ .

RCA treatment and dil. HF dipping & deionized(D.I.) water rinsing were employed for a substrate preparation.

### 3. Results and Discussions

#### —Photoemissivity in the reactant gas—

Influences of the several reactant gases on the photoemissivity were investigated.

Figures 3 and 4 show the change of photoemission with the introduction of reactant gas into the reaction chamber filled with  $\text{H}_2$ .

As shown in Fig. 3, opposite behavior in photoemission was observed between the introduction of  $\text{HCl}$  and  $\text{NH}_3$ . Photoemission increased with the introduction of  $\text{NH}_3$ , while decreased with  $\text{HCl}$ . In view of the surface band diagram, these results imply the type of

surface state generated by the chemical adsorption;  $\text{NH}_3$  generates a surface state of

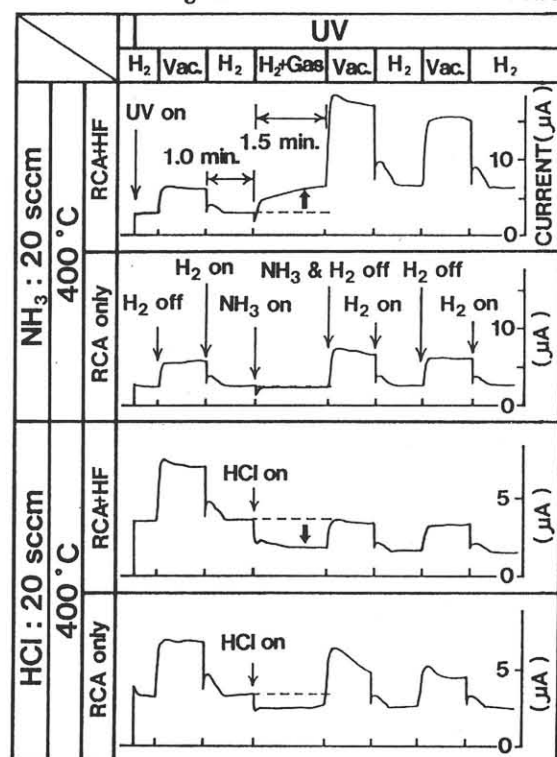


Fig. 3 Change of photoemission with the introduction of reactant gas :  $\text{NH}_3$  and  $\text{HCl}$

donor type and is adsorbed as a positive ion.

On the other hand,  $\text{HCl}$  generates that of acceptor type and is adsorbed as a negative ion. In other words,  $\text{NH}_3$  is adsorbed reductively and  $\text{HCl}$  is adsorbed oxidatively.

Photoemission from the surface once exposed to the reactant gas was not the same as that before exposure even in  $\text{H}_2$  ambient. This is probably due to the surface residual adsorbate in the  $\text{H}_2$  ambient, showing that photoemission is also sensitive to the trace amount of surface contamination.

Difference between  $\text{Si}_2\text{H}_6$  and  $\text{SiH}_4$ , both of which are widely used as Si donation gases, are shown in Fig. 4. It should be noted that, in contrast to the photochemically inactive  $\text{SiH}_4$ ,  $\text{Si}_2\text{H}_6$  is being decomposed photochemically during the measurement.

Though both  $\text{Si}_2\text{H}_6$  and  $\text{SiH}_4$  showed a feature of reductive adsorption, reducibility was shown to be different remarkably.  $\text{SiH}_4$  itself or the thermally derivative

radicals from  $\text{SiH}_4$  was considerably less reductive than that of the photochemically derivative radicals from  $\text{Si}_2\text{H}_6$  even when the thermal decomposition occurred at high temperature. These results seem to give a chemical basis for the success of low temperature photo-epitaxy with  $\text{Si}_2\text{H}_6$ . [2] Highly reductive species in the UV- $\text{Si}_2\text{H}_6$  system probably play an effective role for scavenging the oxidative residual gases or for removing the native oxide after the following equation at the initial stage of Si growth.

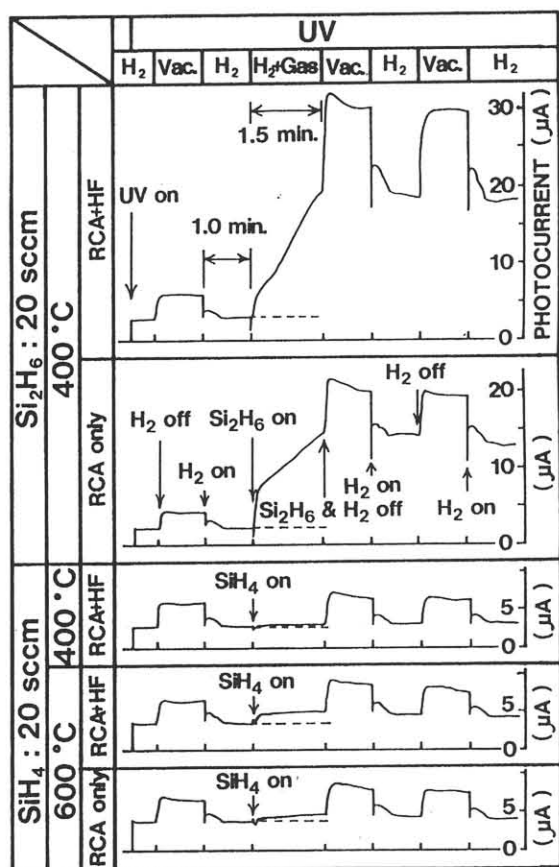


Fig. 4 Change of photoemission with the introduction of reactant gas :  $\text{Si}_2\text{H}_6$  and  $\text{SiH}_4$

#### —Effect of preparation or pretreatment—

A remarkable feature was observed concerning the substrate preparation procedure.

Photoemission from the substrate without HF dipping, or with chemical oxide of 20 Å thick formed during RCA treatment, was insensitive to the change of reactant gas compared with

that with HF dipping. In particular, this feature appeared significantly for the case of  $\text{NH}_3$  as shown in Fig. 3, showing that the chemical adsorption or the decomposition of  $\text{NH}_3$  was strongly catalyzed by a clean Si surface.

By using of this surface-sensitive nature of  $\text{NH}_3$ , effect of several pretreatments was investigated in the  $\text{NH}_3$  ambient.

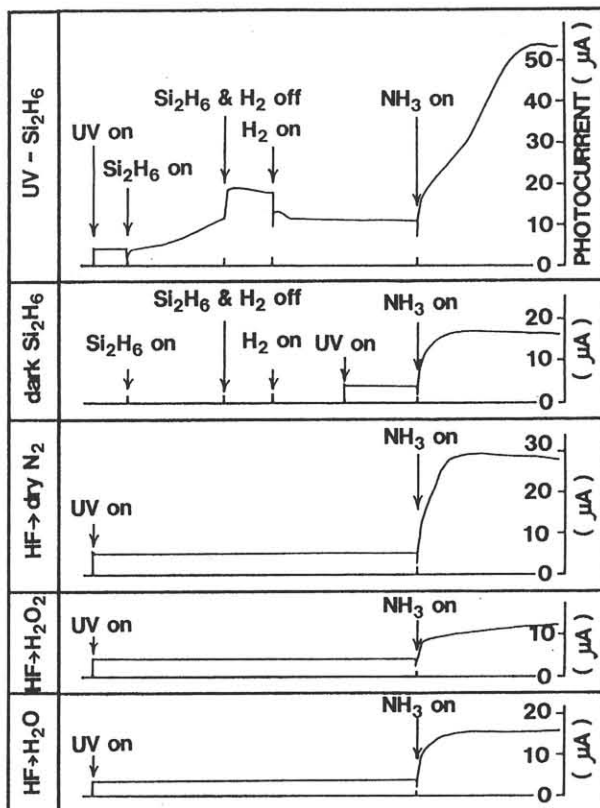


Fig. 5 Effect of pretreatment on the photoemissivity in  $\text{NH}_3$  ambient

Pretreatment examined were  $\text{Si}_2\text{H}_6$  with UV,  $\text{Si}_2\text{H}_6$  without UV, HF dipping without D.I. water rinsing, HF dipping & D.I. water rinsing followed by  $\text{H}_2\text{O}_2$  dipping & D.I. water rinsing as shown in Fig. 5. As seen in this figure, UV- $\text{Si}_2\text{H}_6$  pretreatment made the photoemissivity in the following  $\text{NH}_3$  ambient increase remarkably, implying two possible effects of UV- $\text{Si}_2\text{H}_6$  pretreatment. One is the reductive removal of native oxide by the highly reductive species in the UV- $\text{Si}_2\text{H}_6$  system. And the other is a fresh surface preparation with Si deposition. Though it is not clarified, at

present, which effect is dominant, the former effect should be investigated in detail hereafter as a promising in-situ surface cleaning technique.

In addition to the UV-Si<sub>2</sub>H<sub>6</sub> pretreatment, photoemission in the NH<sub>3</sub> ambient was affected by other pretreatments as shown in Fig. 5.

Pretreatment of HF dipping without the following D.I. water rinsing increased the photoemission to a measurable degree in the following NH<sub>3</sub> ambient, implying that surface with a thinner native oxide was obtained by this pretreatment, or that not a little part of native oxide was already formed during D.I. water rinsing. This result shows the importance of strict management of the D.I. water rinsing procedure. Decrease of photoemission with H<sub>2</sub>O<sub>2</sub> dipping pretreatment is probably attributable to a slight chemical oxidation.

#### —Monitoring of surface reaction—

Reaction systems in which the several reactant gases exist simultaneously were investigated using Si<sub>2</sub>H<sub>6</sub>-NH<sub>3</sub> and Si<sub>2</sub>H<sub>6</sub>-HCl

system as examples. In these systems, competitive adsorption process proceeds between the several sorts of chemical species. Application of photoemission monitoring revealed the correlation of relative intensity of adsorption and redox nature between the reactant gases. Considering the behavior of photo-emission with the sequential switching of reactant gas introduction, shown in Fig. 6, the following characteristics were ascertained; Though Si<sub>2</sub>H<sub>6</sub> was prior to NH<sub>3</sub> on the adsorption, reducibility of Si<sub>2</sub>H<sub>6</sub> was weaker than that of NH<sub>3</sub>. As for the relation between Si<sub>2</sub>H<sub>6</sub> and HCl, it was inferred that the adsorption of Si<sub>2</sub>H<sub>6</sub> was prior to that of HCl.

#### 4. Conclusions

Photoemission from the Si surface adsorbing the reactant gas was used as a probe for in-situ monitoring of the surface chemical process. This method has an advantage that no evacuation or interruption of reaction is needed during measurement, thereby resulting in the observation of surface under the condition that the actual reaction proceeds. Using this monitoring method, the type of surface state generated by the chemisorption of reactant gas was examined; NH<sub>3</sub>, SiH<sub>4</sub> and Si<sub>2</sub>H<sub>6</sub> generated the surface state of donor type, while HCl acceptor type.

This method could also be used for the evaluation of the effect of in-situ surface cleaning or pretreatment using a surface-sensitive ambient such as NH<sub>3</sub>.

#### Acknowledgement

The authors would like to express their thanks to Drs. H. Komiya and H. Abe for their continuous encouragement and managing supports.

#### References

- [1] H. Itoh et al., Extended Abstract of the 1987 fall meeting of E.C.S., p 1069, vol. 87-2, 1987
- [2] T. Yamazaki et al., Extended Abstracts of the 18th Conf. on SSDM, p 213, 1986

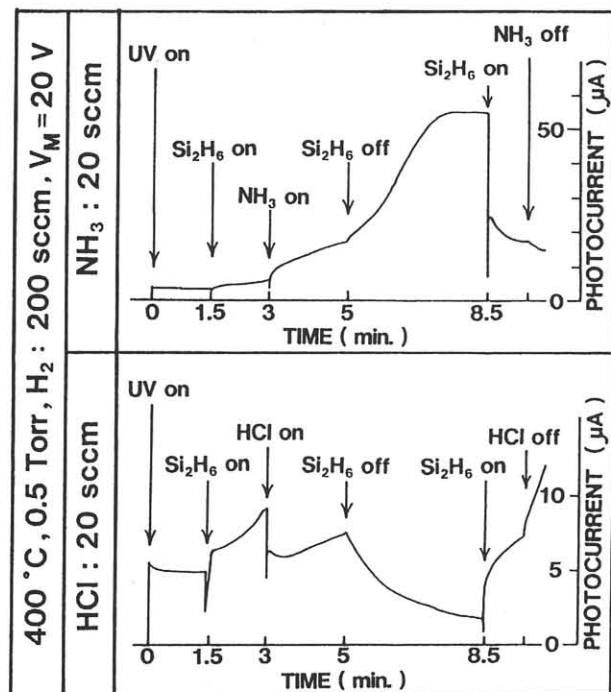


Fig. 6 Photoemission in multi-elementary reaction system : Si<sub>2</sub>H<sub>6</sub>-NH<sub>3</sub> and Si<sub>2</sub>H<sub>6</sub>-HCl