

Surface Analysis for Glass Coating Technology

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The mechanism of glass corrosion phenomena in the air has been clarified by surface analytical techniques so far and can be taken into account at the glass coating process. The OH group on metal oxide thin film on glass can be evaluated by TOF-SIMS and its behavior and formation mechanism is discussed using the O1s chemical shift in ESCA. The application of NMR can make it possible to determine the structure of fluoroorganic molecule coated on glass.

1. Introduction

A glass is a very old material. We find the first description about glass in the literary work of ancient Roman naturalist Pliny at the first century AD. Prior to that people had made use of a glassy obsidian as implements in the stone age.

But recently the use of glass has widely expanded with the advancement of material science. Thus surface coating or treatment to add the new values like optical electrical biochemical function is being extensively carried out to sell glass at higher prices. The outlook of the current glass coating technology

is shown in Table 1. Various materials are coated or surface treated for various purposes using various methods.

To solve the intricate phenomena on surface all sort of analytical technique are made the most of and the comprehensive investigation integrating different types of information should be done to get their marrow. (Table 2)

2. Glass structure

The schematic two-dimensional representation of the structure of sodium-silicate glass is shown in Fig.1[1]. Sodium metals are incorporated as positive ion compensating the

Table 1. The outlook of the current glass technology

Use	Material	Method
Architecture	Solar cut	Metal Oxide Nitride
	Lowreflection	Oxide
	Electromagnetic cut	ITO
	Electrochromic	WO ₃ NiO ITO Ir
	Mirror	Ag/Cu Al Cr
	Contamination-proof mist-proof	TiO ₂ F-compound
Automobile	Solar cut UV cut	Metal Oxide Nitride
	Privacy protection	Metal Oxide Nitride
	Electricheating	Ag Oxide
	Headup Display	Oxide
	Water Repellent	F-compound Silicone
Display	CRT Antireflection Antiglaze	Oxide
	LCD TCO Alkalibarrier	ITO Silica Polyimide
	TFT TCO Metal Colorresist	ITO Silica Cr Polyimide
Media	Magnetic	Cr Pt Co Ni...
Optical	Lens Multicoat	Oxide
	Filter	Oxide
	Photomask Antireflection Shield	Cr CrO CrN...

Table 2. Analytical techniques for glass surface

Subject	Purpose	Method
★ Corrosion	Mechanism Reaction trace	ESCA SIMS IR (ERDA NRA) Isotope: D, ^{18}O -SIMS SNMS ^{17}O -NMR
★ Contamination Contamination-proof	Mechanism Analysis of Contaminant, Reaction Site(Si-OH) Origin Gas Analysis	ESCA TOF-SIMS ESCA TOF-SIMS Chemical Modification RAS Head spaceGC
★ Surface Treatment		
Chemical		
Ion exchange	Structure	ESCA SIMS TOF-SIMS RBS IR RAS Raman Solidstate NMR ESR X-ray Diff. STM AFM SEM TEM EPMA CEM Wet Analysis TG-MS
Dealkalization	Mechanism	
Polish		
Film coating		
Dry process	Structure of Thin Film	
Wet process	Mechanism	

charge balance with so-called non-bridging oxygen. These loose structure and movable cations cause the various surface problems like corrosion, adhesion, ion exchange and so on.

3. Glass corrosion

It has been well known that a glass surface changes by weathering for a long time. But generally a glass surface could be easily renewed by cleaning, so the change on surface did not give significant influence on conventional glass. However when it comes to surface treatment we have to take this into account.

A glass corrodes by the interaction with the atmospheric water and carbon dioxide. The mechanism of corrosion has been supposed to be basically the ion-exchange reaction between alkaline or alkaline earth cations in glass and proton from absorbing water molecule.

This mechanism has been supported by the application of surface analytical methods. Using water enriched with isotope H_2^{18}O , D_2^{18}O the more detailed information can be acquired as to the reaction species[2].

Figure.2 shows the schematic representation of the progress of glass corrosion. Ion-exchange reaction between proton from water molecule and modifier cations proceeds. Cations are leached out to surface and the absorbing water turns to be alkaline side. Consequently the glass network itself begins to

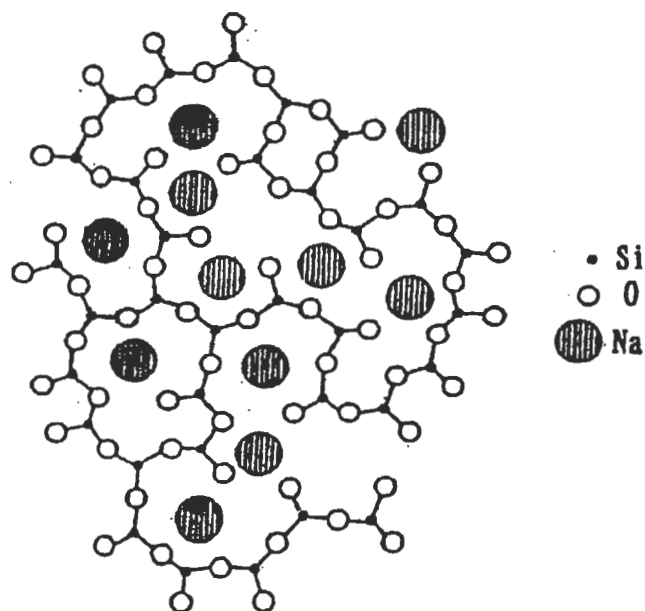


Figure 1. Two dimensional representation of the structure of a sodium-silicate glass

be destroyed.

Finally carbonate which is formed by the reaction between hydroxide of the product of the ion-exchange reaction and atmospheric carbon dioxide is piled on the surface. On the other hand hydrated layer is formed beneath the surface. When the corrosion proceeds to a considerable extent the glass looks hazy and

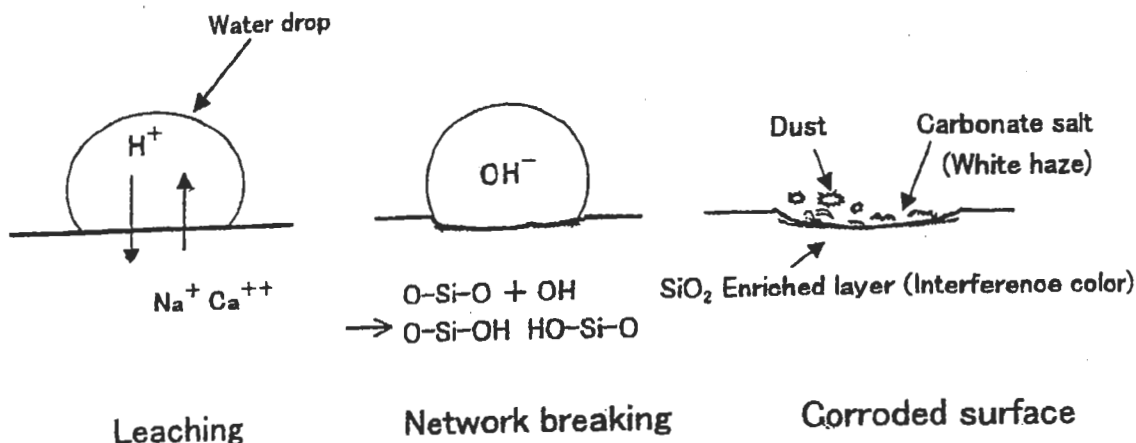


Fig.2 The schematic representation of the proceeding of glass corrosion

shows blue or yellow color by interference.

4. OH group on metal oxide thin film

Besides the compositional change by the corrosion the change on glass surface is also induced from outside, like contamination, absorption, chemical treatment etc..

Figure.3 shows the schematic representation of the organic contamination on glass surface[3].The organic molecules having polar functional group form the hydrogen bond with silanol group on glass surface. Their non-polar portions are oriented outwards and interact with hydrocarbon molecules by Van Der Waals bonding force. Hydrocarbon molecules are piled on them layer by layer. This mechanism has been basically received a support by ESCA or TOF-SIMS measurement. As not only organic contamination but also many other surface phenomena on metal oxide are closely related with OH group, it's a bit important to investigate the function or behavior of surface OH group when we design a chemical treatment or a cleaning process.

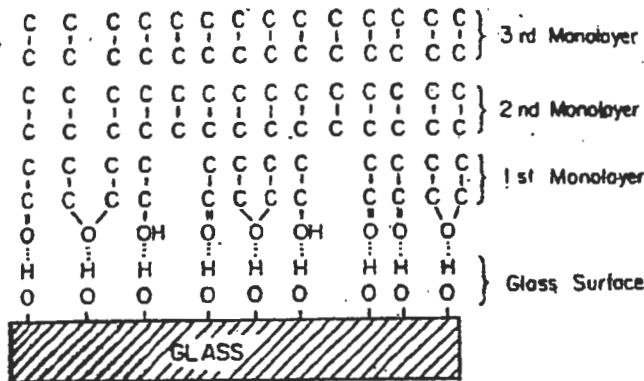


Fig. 3 The schematic representation of the organic contamination on glass.

Figure. 4 shows the change of the contact angle of water on metal oxide thin films sputter- coated on glass with time under 50°C 95%RH.. Each contact angle increases with time and finally reaches a certain saturated level. The saturated level differs with each metal oxide. This difference is proved to be due to the organic contamination absorbing on metal oxide by ESCA measurement as shown in Fig. 5 . The higher the contact angle is the more the carbon from organic contamination is. From these results zirconium oxide seems to

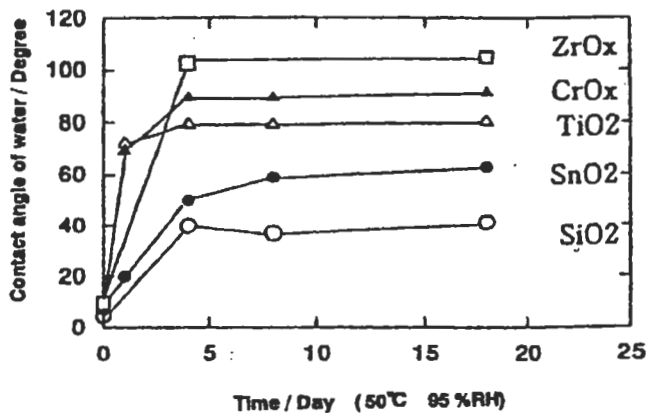


Fig. 4 The change of the contact angle of water on metal oxide thin films on glass with time.

be contaminated most easily and silicon oxide is inclined to be contamination-proof in this series of metal oxides. For this phenomenon OH group is considered to be responsible as reaction site on surface. Surface OH group density could be evaluated by TOF-SIMS

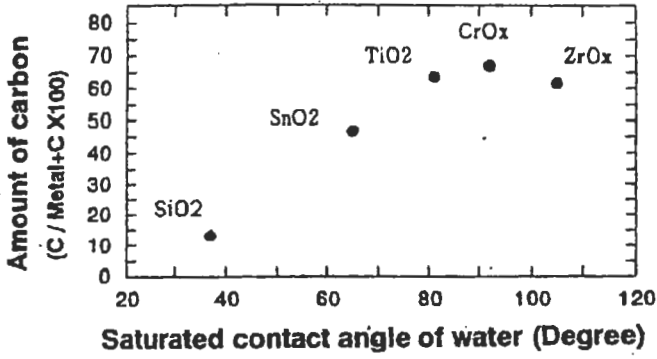


Fig.5 The relation between carbon amount (surface contamination) and contact angle of water

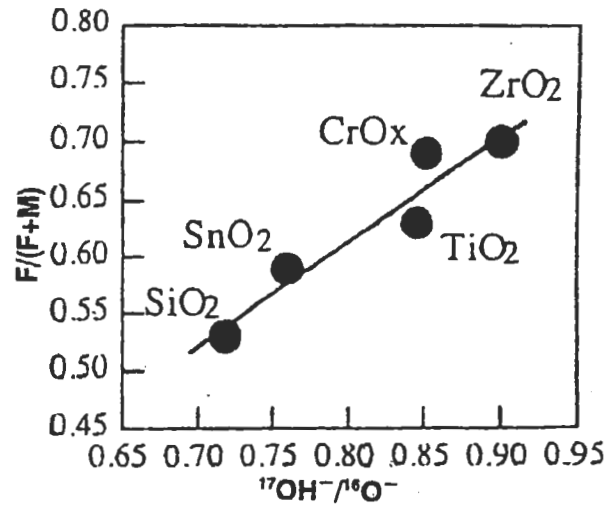


Fig.7 The relation between surface OH amount and the amount of silane coupling agent reacting with metal oxide surface

F/(F+M): Atomic ratio of fluorine and metal measured by ESCA

$^{17}\text{OH}^- / ^{16}\text{O}^-$: SIMS Secondary ion intensity ratio

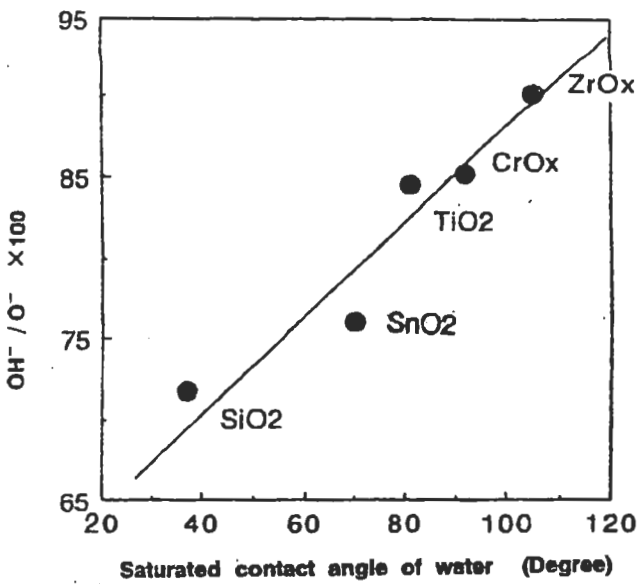


Fig.6 The relation between surface OH amount and contact angle of water

OH^- / O^- : SIMS Secondary ion intensity ratio

using mass number 16 and 17[4].

As shown in Fig.6 the saturated contact angle level has the substantial interrelation with the amount of OH group. From this result the surface reactivity of these oxides seems to be ranked by the density of OH group so zirconium oxide is expected to be treated most easily with chemical agent. Fig.7 shows the reactivity to the silane coupling agent having fluoroalkyl group [$\text{C}_8\text{F}_{17}\text{C}_2\text{H}_4\text{Si}(\text{NCO})_3$]. This kind of treatment is being widely carried out to control the water repellency on thin film. The amount of coupling agent reacting with oxide surface measured by ESCA by detecting fluorine increases according to the order of the OH amount.

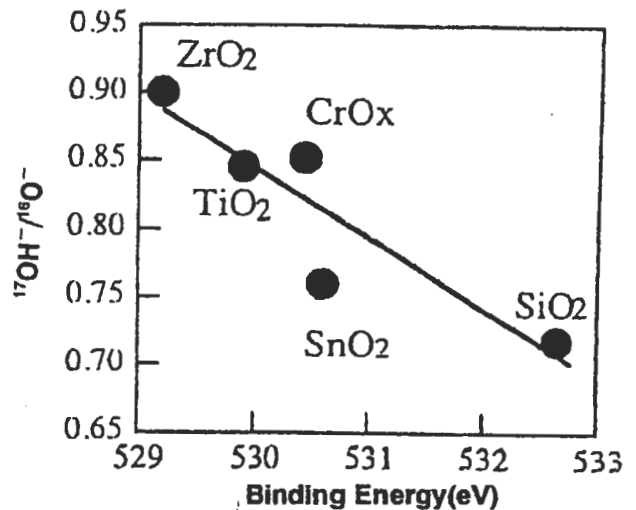


Fig.8 The relation between surface OH amount and O1s binding energy of metal oxide

The reason why the amount of surface OH group varies with each metal oxide can be presumed by considering the formation mechanism of OH group.

Figure.8 shows the mutual relation between the O1s photoelectron chemical shift in ESCA spectrum and the surface OH amount. The O1s chemical shift can be replaced by the electronegativity difference between oxygen and metal ($\Delta \chi_{\text{M-O}}$: M= Si, Sn, Ti, Cr, and Zr) that is an index of the electron density on metal atom as shown in Fig 9. The OH amount increases with the decrease in the electron density on metal. The formation mechanism of OH group on metal oxide surface can be

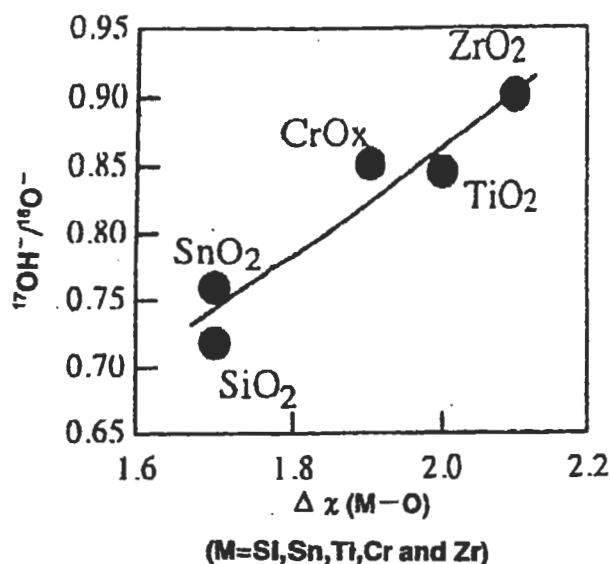


Fig.9 The relation between the OH amount and electronegativity difference

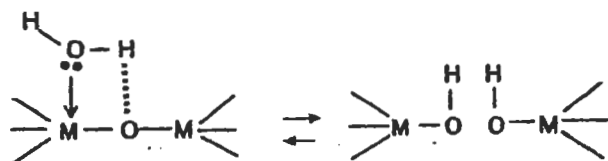


Fig. 10 The mechanism of the formation of OH group on metal oxide

proposed as shown in Fig.10. Absorbing water molecule forms the ring shape precancer with substrate oxide and dissociation follows. The less the electron density on the metal is, the greater the accessibility of the nucleophilic oxygen in water molecule to the metal is. Then the hydrolysis rate is enhanced.

So by measuring O1s binding energy the reactivity of metal oxide thin film on glass can be estimated. This is very useful to design the new composite oxide including more than two metallic elements.

5. Application of various spectroscopies

To solve the surface problem completely we are often tempted to use other analytical method which is not generally placed under the category of surface analytical method.

Vibration spectroscopy or magnetic resonance spectroscopy providing with the information about chemical bonding is very effective especially in the case of organic molecule is a subject. Some contrivances in sample

preparation make it possible to apply these spectroscopies to surface problems.

Nonconductive silicon wafer is well known as the substrate to get IR spectrum of thin film for example. NMR or ESR spectrum can be got by using the very thin glass sheet of around $50 \mu\text{m}$ thickness as substrate of thin film that is produced as the cover of the solar cell mounted on an artificial satellite.

As the example of the application of the spectroscopy which is not a surface analytical method, the structural analysis of the fluoro organic molecule on the water-repellent glass for automobile by solid NMR is taken here[5]. This type of glass is already practically used for front side glass or out side rear view mirror to keep the clear view in rainy day and is being developed aiming at the wiperless windshield. To get the high water repellency and to make water droplet easily removed the silane coupling agent having perfluoroalkyl chain is coated on glass as shown in Fig.11. The sol-gel silica film with high density silanol group is coated in advance as an undercoat layer to increased the reaction site.

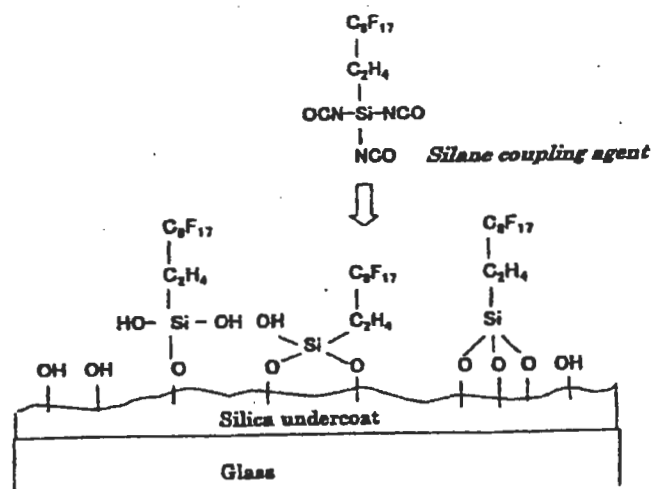


Fig.11 The water-repellent treatment of glass

Because a very tough simulating test like up and down cycle with muddy water waits for this glass at carmakers it is important to know what type of bond is formed and what type of bond is desirable against a durability test.

For this purpose ^{29}Si NMR was useful. ^{29}Si NMR provides us with the information about the structure of silicate units connectivity. In

this case the powdered sol-gel silica was coated with silane coupling agent and NMR spectrum could be measured. From spectra the main bonding form could be determined for each coating condition or the structure of coupling agents. Using this information the most suitable structure of silane coupling agent or coating condition could be designed.

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