Effects of Surface Pretreatments of a Glass Substrate on the Properties of Tin Oxide Film Prepared by Plasma-Assisted Chemical Vapor Deposition

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(Received October 9, 1991)

Synopsis. A glass substrate was modified by thermal and chemical treatments with a fluoride solution and molten potassium salt. These surface treatments were found to affect both the electroconductive and optical properties of tin oxide film prepared by plasma-assisted chemical vapor deposition.

The formation and properties of thin films are affected by the physical and chemical natures of the substrate surface used[1,2] and, therefore, surface treatments would be effective for modifying thin solid films deposited on them. The usefulness of such treatments has been studied in the present work for a glass substrate on which a tin oxide film is to deposit by plasma-assisted chemical vapor deposition (PCVD). Tin oxide film is well-known as a transparent electroconductive film, and has been used as a first test material.

A few previous studies have shown that thermal and chemical treatments of silicon oxide, aluminium oxide, and other substrates enhance the dispersion of Group-VIII metals deposited by vacuum evaporation on them.[3–5] For fine metal particles prepared on high-surface-area substrates by wet processes, several studies have indicated the effectiveness of their surface pretreatments for improving the dispersion and catalytic activity of the supported particles.[6–14] Although a variety of surface treatments have been reported for solid materials to modify their own functions as catalysts and adsorbents,[15,16] only a few studies have so far applied those treatments to substrate materials for regulating the function of fine particles and thin solid films on them.

Experimental

The substrate used in the present work was a soda-lime glass plate (25 mm×25 mm×1 mm) supplied by Matsunami Glass Ind., Ltd. It was cleaned with detergents and distilled water, air-dried at 100 °C, and then subjected to the surface treatments described in Table 1. Those treatments are hereinafter referred to as H, F, and K, described in Table 1. The substrate surfaces were examined with photoelectron spectroscopy (XPS, Shimadzu ESCA-750) and scanning electron microscopy/X-ray microanalysis (SEM/XMA, Hitachi S-530S/Horiba EMAX-1500).

Table 1. Surface Treatments for a Glass Substrate

Treatment[a]	Procedure
Thermal (H)	Heating in air at atmospheric pressure and 425 °C for 1 h.
Chemical, with fluoride (F)	Immersion in an aqueous solution of 10%NH_4F+2%H_2SO_4 at room temperature for 5 h, washing with distilled water, and heating in air at 450 °C for 1 h.
Chemical, with molten potassium salt (K)	Immersion in molten potassium nitrate at 400 °C for 4 h with a crucible in ambient atmosphere

a) Letters H, F, and K in parentheses are abbreviations for the treatments.

In PCVD, $Sn(CH_3)_4$ vapor was the starting material, and was decomposed with a d.c. glow discharge onto substrates in a glass chamber, in which two electrodes were separated by about 3—5 cm; the substrate on an electrical heating plate was positioned near to the anode. The temperature of the substrate was measured with a thermocouple attached to its surface before PCVD was carried out. The chamber was evacuated to less than 3 Pa and the vapor was introduced to 13—40 Pa from a reservoir at ambient temperature. PCVD was conducted with an applied voltage of 1—2 kV for 30 min in order to prepare transparent thin films a few hundreds namometers thick; they were then calcined in air at 500 °C for 30 min.

The sheet resistances of the thin films prepared were measured by a two-probe method using peripheral surface electrodes in an air-conditioned room. For a given film, five data points were collected for five different locations at the same distance. The five data points were in agreement, with errors smaller than ±10%; the mean value of these was used as a representative for the film measured. The sheet resistivity was obtained from a predetermined relationship between the resistivity measured by the two-probe method and that measured with two parallel electrodes for the same film samples. The optical properties were measured by ellipsometry with a ray of monochromatic light of 546 nm (Mizojiri DV-36S). The refraction index was first determined using the Abelès method;[19] the film thickness was then found from the determined refraction index. Ellipsometry was also performed in an air-conditioned room. The state of the surface layers was examined by the XPS and high-resolution scanning electron microscopy (HRSEM, Hitachi S-900).

Results and Discussion

Table 2 gives the XPS results for the substrates. The K-treatment caused a partial exchange of potassium

Table 2. XPS Results[a]

Element	Treatment		
	un[b]	F	K
Si 2p	100	100	100
Na KLL	107	97	85
K 2p	60	56	92
Mg 2s	15	14	15
Ca 2p	5	5	7
F 1s	—	c)	—

a) Relative intensities to Si after the intensity corrections. b) Untreated. c) Signal within the noise level.

ions for sodium ions, as expected. The F-treatment was expected to introduce fluorine species onto the surface by displacing the surface hydroxyl groups,[17,18] even though XPS did not give any information about this. The dissolution of glass in the F-treating solution could be prevented by adding sulfuric acid. SEM/XMA showed that the H-treatment did not affect the chemical species in the surface layer; however, it probably had an effect on removing the surface hydroxyl groups as well as strongly adsorbed water molecules. All of the treatments performed had chiefly chemical effects on the substrate.

Table 3 shows the physical properties of tin oxide films deposited at 150 °C. The sheet resistivities for H- and K-treated substrates were comparable to one another and smaller by roughly one order of magnitude than those for F-treated and untreated substrates. The thin films on the former two substrates indicated smaller specific resistivities and larger refraction indices compared with those on the latter two. No significant difference in the binding energy of Sn3d was found among the films on the three treated substrates, and their binding energies were slightly higher than that for the untreated substrate. The observed binding energies were higher by about 0.5 eV than that reported for tin dioxide,[20] and the oxidation number of tin in the PCVD films prepared was higher than that in bulk tin dioxide.

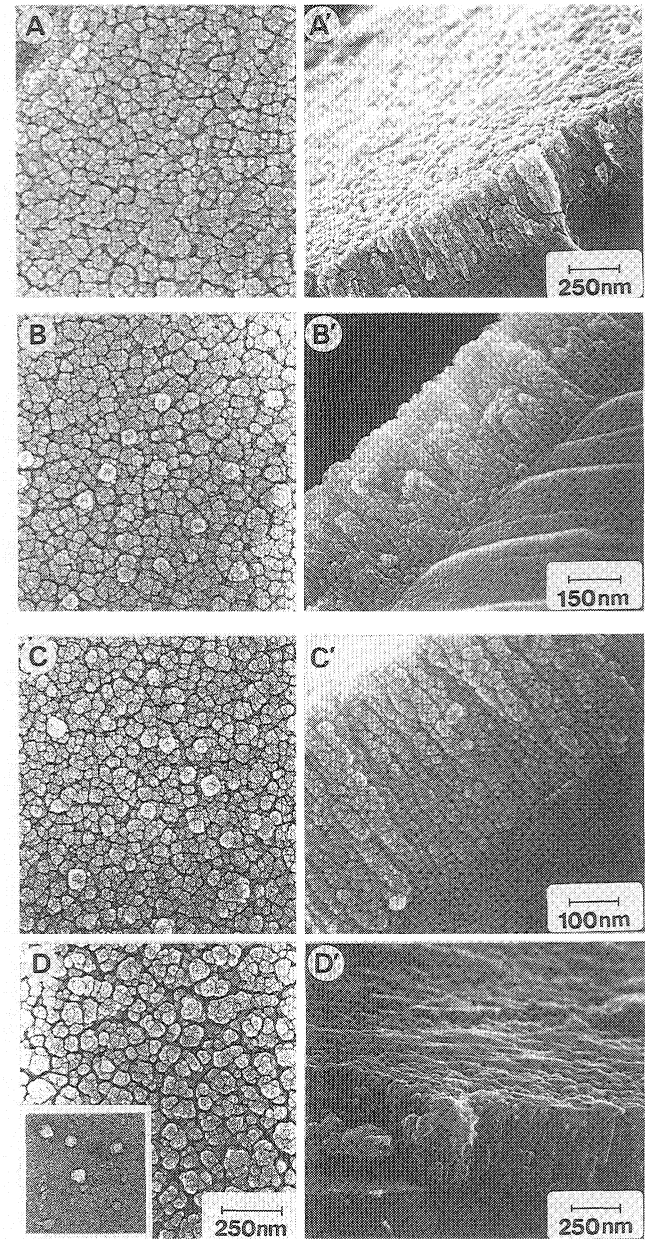

Fig. 1. HRSEM micrographs of tin oxide films on untreated (A,A′), H-treated (B,B′), F-treated (C,C′), and K-treated (D, D′) glass substrates. Very fine particles smaller than 10 nm in diameter can be seen; these are platinum particles which were sputtered onto the oxide films for clearer imaging.

When PCVD was performed onto substrates that were not heated, the sheet resistivities of the prepared tin oxide films were similar, being of the order of 1.0×10^4 $\Omega/\square$; we observed little effect of substrate pretreatments.

Figure 1 shows HRSEM micrographs of the top and fracture surfaces of tin oxide films on the substrates at 150 °C, indicating slight differences in the structure among them. Grains of 20—100 nm in size and grain boundaries of less than 10 nm in width can be seen in the top views. The grains on F-treated substrate seem to be larger than those on the others. The coalescence of grains is the most pronounced on the untreated substrate. For the film on a K-treated substrate, very large grains of 150—400 nm in size exist with a number density of about 6 grains $\mu\mathrm{m}^{-2}$. Side views show the growth of columns that are roughly 50 nm wide for all of the films. A lateral growth of the columns can be seen, and its extent is smallest for the film on an F-treated substrate.

The present results have demonstrated that pretreatments of a glass substrate affect both the electroconductive and optical properties of a tin oxide film deposited by PCVD. Significant effects were observed when the substrate was kept heated at 150 °C on the PCVD while little effect when the substrate was not heated as described above. The mechanism of PCVD film formation in our cases is not clear at present; however, the difference in the effects between heated and unheated substrates may be related to the surface mobility of chemical species that form in the gas phase and is adsorbed on the substrate. On the unheated substrate the surface mobility may be low and the nucleation would take place at any sites, even though these have weak interactions with the surface-moving species. On the heated substrate, in contrast, the mobility may be high and nucleation would occur on the sites having strong interactions with the surfcae-moving species; the effects of substrate pretreatment have appeared in this case. It is supposed that the initial stage of PCVD film formation depends on the state of the substrate surface, and that it is sensitively affected by the substrate treatment. This effect remains throughout the subsequent film growth; the treatments still have an effect on the properties of the resulting films in spite of their great thickness, being as large as 200 nm. In general, the effect of a surface treatment depends on the method of film deposition. It will be interesting to examine the effects of the substrate treatments studied in the present work for other depositions, for example, vacuum evapo-

Table 3. Characterization of a Tin Oxide Film Deposited by PCVD

Treatment	Sheet resistivity	Film thickness	Specific resistivity	Refraction index	E_b(Sn3d)
	$10^5 \Omega/\square$	nm	Ω cm	(−)	eV
Untreated	12.0	248	30	1.84	—
	18.0	264	48	1.81	486.75
	18.0	—	—	1.82	—
H	1.6	241	4	1.93	486.90
	1.7	217	4	1.87	—
	1.9	—	—	—	—
F	25.0	217	54	1.81	486.90
	17.0	248	42	1.84	—
	12.0	253	30	1.82	—
K	3.5	236	8	1.88	486.95
	2.3	240	6	1.93	—
	4.2	244	10	1.83	—

ration and the so-called sol-gel method,[21] as well as other chemical treatments.

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