Strength Evaluation of Borosilicate Glass Coated with Thin Ceramic Films by Radio-Frequency Sputtering

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1. Introduction

In recent investigations, it is reported that glass sputtered with ceramic thin film is functionally used as magnetic/electronic device materials [1-3] as well as optical ones [1, 4-7]. In functional usages and/or mechanical applications of coated glass materials, the information on strength of such materials is also required to guarantee the integrity during service.

In this study, strength properties of a borosilicate glass coated with alumina, silicon carbide, or titanium nitride were experimentally investigated to clarify the difference in the properties attributed to material kinds of ceramic coating. A radio-frequency (RF) magnetron sputtering method was adopted in producing thin ceramic films on glass. Coated glass materials were prepared by changing a combination of RF output power and film thickness for each ceramic coating material. Roughness and hardness of coating ceramic film are recognized to be important factors for tribological usage [8]. So, roughness and hardness were also measured as surface properties which may affect the strength of coated materials. Since tensile tests of brittle glass or ceramic materials are very difficult to be performed in adequate evaluation of their strength characteristics [9], bending tests of the glass coated under several conditions were conducted instead of tensile tests in this work. The dependencies of strength properties of coated materials on the thickness of ceramic film and on the RF output power were also investigated to clarify a suitable sputtering condition. Finally, a new procedure to estimate the strength of coated glass was proposed by using the surface properties of coating film as well as sputtering time, and its applicability was discussed in comparison with experimental results.

2. Experimental Procedures

2.1 Material Processing

A commercial borosilicate glass was used as a substrate material. Alumina (Al_2O_3) of 99.99% purity, silicon carbide (SiC) of 99.8% purity, and titanium nitride (TiN) of 99.0% purity were adopted as target materials. The geometry of glass substrate was a disk type with a diameter of 100mm and a thickness of 2mm. In the present work, each ceramic film was coated by sputtering as mentioned below, and the thickness t_f of coated film was controlled to be 1μm, 3μm or 5μm.

An RF magnetron sputtering apparatus of upper deposit type was used in the coating process. The distance between substrate and target materials was set to be 40mm in this apparatus. Metallic supporting or bonding plates, on which substrate and target materials were fixed respectively, were being water-cooled during the processing. Before starting a steady sputtering, pre-sputtering was carried out for 300s so that a contaminated layer of target material could be removed. The initial degree of vacuum in a processing chamber was kept less than 1.3×10^{-4}Pa. The flow-rate and pressure of argon gas, which was used to activate the sputtering process in the chamber, was controlled to be 167mm^3/s and 1.3Pa, respectively. In sputtering of ceramic target materials, the initial temperature of substrate was not controlled, and two levels of RF output power P were selected as P = 400W and 600W.

2.2 Measurements of Film Surface Characteristics

Images of surface-areas on each coating film were taken through a laser scanning microscope (LSM), and the images were processed into digital data by using a personal computer in which software for image-processing was installed. Data in individually measured areas were used to evaluate porosity and roughness of their respective areas by using the images processed by the software. The center-line-average roughness, R_a, was measured as the roughness of specimen surface in this work.

The surface hardness of coated materials is one of important factors in characterizing the strength of coated materials. To avoid the influence of the substrate hardness on the film hardness, it has been recommended that a penetrating depth D of indenter should be kept one-tenth or one-fifth of the film thickness [10]. For this situation, a dynamic microhardness tester, which has a triangular pyramid and an available range of indentation force F from 98μN to 1.96N, is appropriate to measure the film hardness. It has been found that the aforementioned condition is properly satisfied in ceramics coated materials by using a dynamic microhardness tester [11, 12]. The dynamic microhardness H is defined as

$$H = 371\left(\frac{F}{D^2}\right) \qquad (1)$$

In Eq. (1), units of H, F and D are respectively GPa, N and m.

2.3 Bending Test

For bending tests, plate type specimens with dimensions of 10mm in width and 40mm in length were cut out from coated materials and the glass substrates.

In evaluating bending strength, a three-point or four-point bending test is usually adopted. In this work, a three-point bending test is used to achieve more reduction of friction points in a supporting system. The span length in three-point bending test was 20mm. The loading rate was controlled so that the rate of nominal stress at the position subjected to the maximum tensile stress in a specimen should be 100MPa/s. In setting a coated specimen on supporting equipment, the coated surface of the specimen was located in the tensile side. Fifteen specimens were prepared for each sputtering conditions. All tests were carried out in an ambient atmosphere, i.e., at temperature of 294±6K and in relative humidity of 73±2%. The bending strength of coated and non-coated specimens was calculated as the maximum nominal stress, which was monitored at final failure, irrespective of the actual breaking position.

3. Experimental Results and Discussions

3.1 Characteristics of Coating Film

The observation by LSM revealed that the average of porosities measured on surfaces of coated ceramic films was less than 0.1%. The result suggested that sufficiently dense films were formed under the sputtering conditions adopted in the present work.

Table 1 summarizes statistical parameters of surface roughness R_a measured on coated ceramic films. In the table, the coefficient of variation is also indicated as a reference factor of statistical scatter by being abbreviated to COV. The parameter COV is defined as the standard deviation divided by the mean value. Larger COV is corresponded to larger scatter. Compared with the mean surface roughness of glass, $R_a = 3.92\times10^{-2}$μm, the surface coated with ceramics in any case is clearly rougher than the glass surface. The roughness of coated film is found to increase with increasing the film thickness. It is well recognized that such a tendency is caused by a shadowing effect during a coating process of physically vaporized deposit type. As a whole trend in Al_2O_3 or TiN coated materials, the surface coated under lower RF output power P is smoother than the surface coated under higher power. In SiC coated materials, however, the film roughness does not always change systematically with respect to P. As seen in Table 1, thicker TiN films formed under higher P are particularly rougher than films of the others. Since COV values of surface roughness on coated glass are around 2×10^{-1} as indicated in Table 1, a scatter of roughness is almost the same independently of film material and coating condition. COV values of roughness measured on coated films are a little smaller than COV = 2.41×10^{-1} in substrate roughness.

Table 1(a). Surface roughness R_a on coated Al_2O_3 film.

RF output power	Film thickness t_f	1μm	3μm	5μm
P = 400W	Mean of R_a (μm)	4.63×10^{-2}	4.83×10^{-2}	5.19×10^{-2}
	COV	1.94×10^{-1}	2.36×10^{-1}	1.83×10^{-1}
P = 600W	Mean of R_a (μm)	5.26×10^{-2}	5.77×10^{-2}	6.44×10^{-2}
	COV	2.07×10^{-1}	2.01×10^{-1}	1.79×10^{-1}

Table 1(b). Surface roughness R_a on coated SiC film.

RF output power	Film thickness t_f	1μm	3μm	5μm
P = 400W	Mean of R_a (μm)	6.11×10^{-2}	6.69×10^{-2}	6.73×10^{-2}
	COV	1.75×10^{-1}	1.59×10^{-1}	1.71×10^{-1}
P = 600W	Mean of R_a (μm)	6.28×10^{-2}	6.57×10^{-2}	6.04×10^{-2}
	COV	1.60×10^{-1}	1.85×10^{-1}	1.66×10^{-1}

Table 1(c). Surface roughness R_a on coated TiN film.

RF output power	Film thickness t_f	1μm	3μm	5μm
P = 400W	Mean of R_a (μm)	6.66×10^{-2}	6.00×10^{-2}	7.12×10^{-2}
	COV	2.28×10^{-1}	1.83×10^{-1}	2.81×10^{-1}
P = 600W	Mean of R_a (μm)	6.60×10^{-2}	8.47×10^{-2}	9.23×10^{-2}
	COV	2.06×10^{-1}	1.62×10^{-1}	1.73×10^{-1}

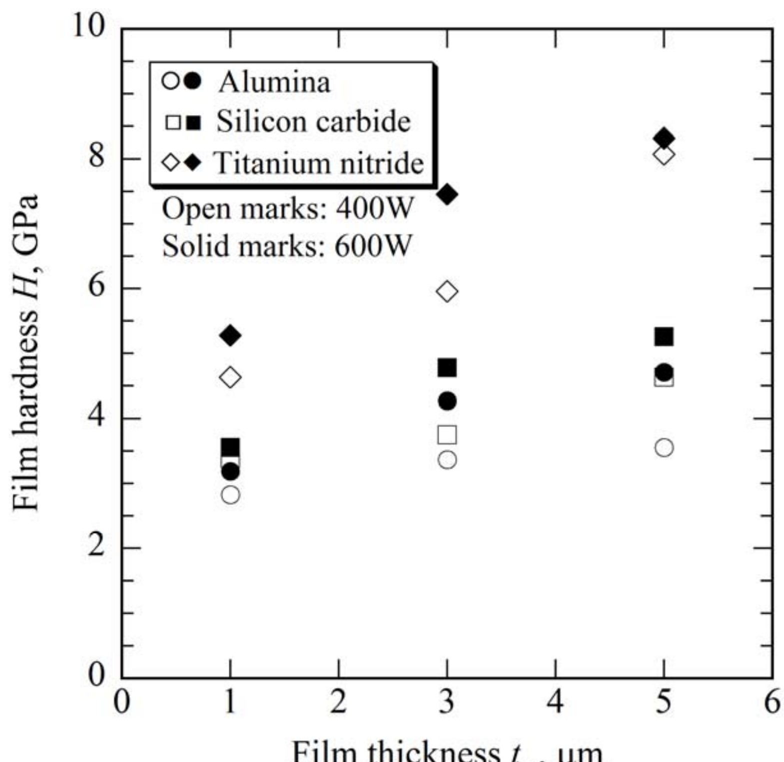

Fig. 1. Hardness of coated ceramic film correlated with film thickness.

Film hardness H measured as a dynamic hardness is correlated with film thickness in Fig. 1. Since the mean value of dynamic hardness of the glass substrate is 2.21GPa, every coated film is found to be harder than the substrate glass. It is revealed, however, that COV values of hardness measured on coated films are larger than those in the substrate hardness. This implies that the hardness of coated films has a larger dispersion compared with that of the glass substrate. In each ceramic film, thicker film has higher hardness, because the influence of the substrate hardness, which is softer than those of coated ceramic films as aforementioned, is reduced in thicker film. It is also clarified that the surface hardness of films coated under a higher RF power *P* is larger. It is suggested that higher RF power brings denser film.

3.2 Strength properties of coated material

It is well known that a large dispersion is often observed in the strength of brittle materials. At first, statistical properties of strength σ_f are investigated. When strength distributions are plotted on Weibull probability papers, the strength distributions of all coated glass are found to shift toward higher strength region compared with the strength distribution of the glass substrate. This implies that the strength of glass is improved by ceramic coating even if the dispersion of strength is considered. It is also revealed that the strength distributions are well approximated by the two-parameter Weibull probability function which is expressed as Eq. (2).

Table 2. Statistical parameters of bending strength.

(a) Alumina coated glass				
RF output power	Film thickness t_f	1μm	3μm	5μm
P = 400W	Coefficient of variation	0.166	0.157	0.152
	Shape parameter m	7.41	7.51	6.97
	Scale parameter σ_S (MPa)	99.2	113	111
P = 600W	Coefficient of variation	0.131	0.119	0.195
	Shape parameter m	8.81	8.84	5.45
	Scale parameter σ_S (MPa)	120	127	112
(b) Silicon carbide coated glass				
RF output power	Film thickness t_f	1μm	3μm	5μm
P = 400W	Coefficient of variation	0.121	0.139	0.124
	Shape parameter m	9.14	7.58	9.13
	Scale parameter σ_S (MPa)	105.2	113.9	106
P = 600W	Coefficient of variation	0.150	0.131	0.126
	Shape parameter m	7.50	8.41	9.70
	Scale parameter σ_S (MPa)	110	120	109
(c) Titanium nitride coated glass				
RF output power	Film thickness t_f	1μm	3μm	5μm
P = 400W	Coefficient of variation	0134	0.155	0.204
	Shape parameter m	8.37	7.55	5.74
	Scale parameter σ_S (MPa)	106	112	126
P = 600W	Coefficient of variation	0.149	0.138	0.208
	Shape parameter m	7.42	8.49	4.82
	Scale parameter σ_S (MPa)	120	123	137

$$F(\sigma_{\mathrm{f}}) = 1 - \exp\left\{ -\left(\frac{\sigma_{\mathrm{f}}}{\sigma_{\mathrm{S}}} \right)^{m} \right\} \tag{2}$$

In the above equation, σ_S and m are respectively the scale and shape parameters. The shape parameter is referred to as Weibull modulus, when the parameter is determined by approximating a strength distribution by two-parameter Weibull probability function. The shape parameter m, as like as COV, is also associated with a range width of scatter; i.e., smaller m is corresponded to larger scatter. The statistical parameters of bending strength are summarized in Table 2. As seen in Table 2, COV increases and m decreases for thicker film in TiN coated glass. This implies that, in TiN coated glass, the strength scatter increases as the film thickness becomes thicker. On the other hand, COV and m do not clearly depend on the film thickness in Al_2O_3 or SiC coated glass.

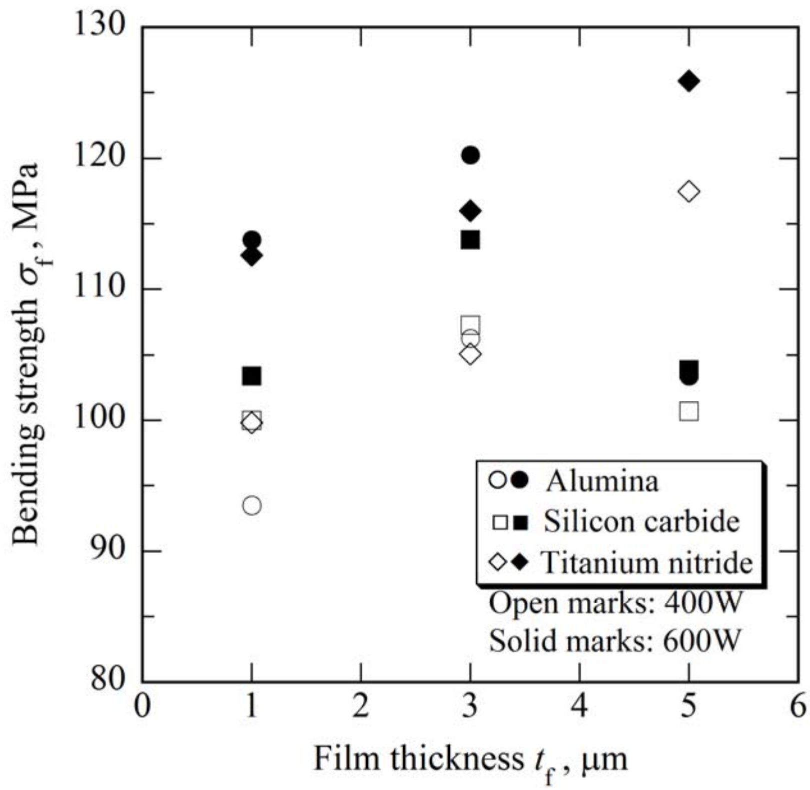

Fig. 2. Strength correlated with thickness of coated film.

The mean strength σ_f is correlated with the thickness t_f of coating film in Fig. 2. As for TiN coated glass, it is found that the strength increases monotonically as the film thickness is increased. On the other hand, it seems that the strength in Al_2O_3 or SiC coated glass has a peak around a film thickness of 3μm. It is speculated that such an anomalous behavior may be attributed to a competition between two phenomena as follows. The strength may be improved by coating of hard ceramic film, whereas the strength is probably degraded by softening of substrate which is caused by heating during long-time sputtering process. Therefore, in the next section, a strength evaluation will be discussed by considering the sputtering time as well as the surface properties of coated film such as hardness and roughness.

4. Estimation of Strength Improvement by Ceramic Coating

A higher hardness of coating film on specimen surface is considered to improve the strength of coated glass under loading mode of a bending type. Actually, the proportional relationship of the strength to the hardness is well recognized in metallic materials. In ceramic materials too, a similar relation has been reported elsewhere [14]. On the analogy of such an empirical fact as aforementioned, it is suggested that the strength may be proportional to the film hardness.

On the other hand, in an infinite plate, a fracture mechanics criterion for brittle material including a crack is described as follows.

$$\sigma_{\mathrm{f}} (\pi a)^{1/2} = K_{\mathrm{C}} \tag{3}$$

In the above equation, σ_{f} and a are respectively the strength of the plate and the half length of the crack. Another parameter K_{C} is a constant toughness, when it is obtained by a fracture toughness test using a specimen with sufficiently long crack. The criterion (3) can be rewritten as

$$\sigma_{\mathrm{f}} = K_{\mathrm{C}} (\pi a)^{-1/2} \tag{4}$$

Equation (4) implies that the strength is proportional to the inverse of root square of the flaw size. Considering surface roughness as a kind of surface flaw, it is presumed that strength is proportional to the inverse of root square of roughness.

By the way, it is found that the strength decreases for longer sputtering time irrespective of the RF output. Longer sputtering time raises temperature of coated material including glass substrate. Concerning glass substrate, the sputtering process is equivalent to the subjection to a heat treatment. Therefore, the temperature elevation results in the softening of glass substrate. This may be supported by a fact that the glass softening is observed after a heat treatment by elevating the initial substrate temperature in the chamber of sputtering apparatus [13]. In the present estimation, a function of exponential type is assumed as one of functions which can express such a strength degradation with respect to the sputtering time τ; i.e., a function $\exp(\beta\tau^{\gamma})$ is considered as a simple form. The parameters β and γ in the exponential function are negative and positive constants, respectively. This function represents a phenomenon as follows; there is no strength degradation at the beginning of sputtering with τ = 0, though the degradation occurs during sputtering process with $\tau > 0$. It should be noted that the exponential term is determined by the sputtering time and the kind of substrate glass independently of coating film materials.

Consequently, a new procedure to estimate the rate of strength improvement (σ_c/σ_s) by ceramic coating is proposed by incorporating relative hardness (H_c/H_s) and roughness (R_{ac}/R_{as}) with sputtering time τ in a time unit of ks. Subscripts "s" and "c" imply respectively parameters related with substrate glass and coated glass. Finally, an estimation of strength improvement by coating is proposed as follows.

$$\frac{\sigma_c}{\sigma_s} = \alpha \left(\frac{H_c}{H_s}\right)\left(\frac{R_{ac}}{R_{as}}\right)^{-1/2} \exp\left(\beta \tau^{\gamma}\right) \quad (5)$$

The parameters, α, β and γ, are finally determined by the most suitable fitting, and their values are summarized in Table 3.

Table 3.Parameters in estimating strength.

Film material	α	β	γ
Alumina	1.10	–0.0713	1.16
Silicon carbide	1.03		
Titanium nitride	0.838		

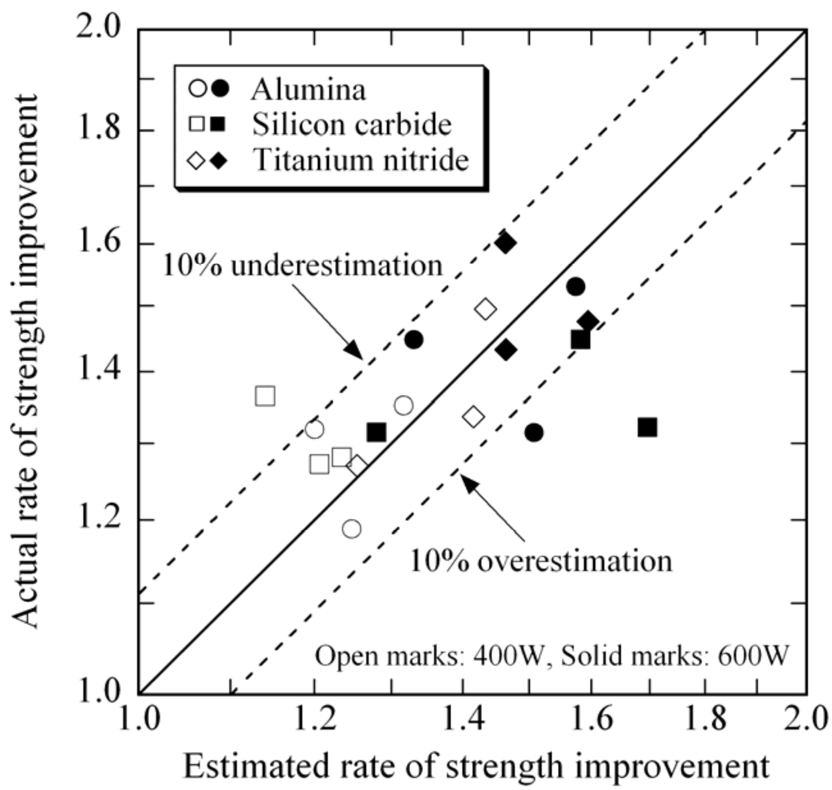

Fig. 3. Estimation of strength improvement by ceramic coating.

As mentioned previously, the parameters β and γ are the same irrespectively of film materials. In Eq. (5), the parameter α should be unity considering the situation of no sputtering, because σ_c is equal to σ_s as a result of $H_c = H_s$, $R_{ac} = R_{as}$, and $\exp(\beta\tau^{\gamma}) = 1$ with $\tau = 0$. As seen in Table 3, however, the α-value deviates a little from unity, and it depends on a combination of substrate and coating materials.

The rate of strength improvement observed in experiments is correlated with that estimated by using Eq. (5). Figure 3 shows the comparison between both values of strength improvement rates in a logarithmic graph. In the figure, broken lines indicating the deviation of ±10% from the exact estimation are also drawn. As seen in Fig. 3, most of all data are well estimated within ±10% by using the proposed procedure, even though each ceramic coating is produced under six different sputtering conditions.

5. Concluding Remarks

The improvement in durability of coated glass is desired in practical applications of such a material. In this work, the effect of coating material kind was evaluated on strength properties of coated glass. Main results are as follows.

The borosilicate glass was actually coated with three ceramic materials; i.e., alumina, silicon carbide and titanium nitride. The coating was processed by the radio-frequency (RF) magnetron sputtering method under two different RF output powers. Mechanical properties of coated materials were investigated with respect to the thickness of sputtered ceramic film. By measuring surface roughness and porosity on coating film, it was found that relative smooth and dense coating films were produced irrespective of the sputtering condition examined in this work. The hardness of coating film was measured by using a dynamic microhardness tester. Observations in hardness test revealed that the coating film became harder for thicker film and/or higher RF output power. Strength tests of coated materials were also conducted under three-point bending mode. The strength properties of ceramics-coated materials were improved in comparison with those of the glass substrate. It was found that the film hardness became higher and the strength was increased in thicker films. To estimate a rate of strength improvement by ceramic coating, a new procedure was proposed by incorporating relative hardness and roughness with sputtering time. The rates of strength improvement in experiments were well estimated by using the proposed procedure.

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