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Structural dependence of corrosion resistance of amorphous carbon films against nitric acid☆

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ABSTRACT

To investigate the structural dependence of the corrosion resistance of amorphous carbon (*a*-C:H) films, three different types of *a*-C:H films etched by nitric acid were evaluated using a surface plasmon resonance (SPR) device with a multilayer structure consisting of an *a*-C:H layer on Ag. Two non-hydrogenated amorphous carbon (*a*-C) films and one hydrogenated *a*-C:H film were synthesized to estimate the effects of the sp^2/sp^3 ratio and hydrogenation, respectively. A flow cell for the introduction of nitric acid solution was placed on the amorphous carbon layer of the multilayer structure. A 0.3 mM nitric acid solution was used in the etching tests. The Kretschmann configuration was used for SPR measurement, and the SPR angle was determined as the angle with minimum reflectivity. The SPR angle decreased with increasing duration of nitric acid injection into the flow cell, indicating that the film was corroded by the nitric acid. The thickness of the films was calculated from the SPR angle. The rates of decrease in the thickness were 2.2, 0.8, and 1.6 nm/h for the *a*-C films with lower and higher sp^2 contents and the 17 at.% hydrogenated *a*-C:H film, respectively. Although the hydrogen content had little effect on the rate of change in the film thickness, the film thickness clearly decreased with decreasing sp^2/sp^3 ratio. These results indicate that the sp^2/sp^3 ratio is an important factor determining the chemical resistance to nitric acid solution.

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1. Introduction

Hydrogenated amorphous carbon (*a*-C:H) films have been applied to mechanical parts owing to their high hardness and low friction coefficient [1–3]. It is well known that these mechanical properties depend on the structure of the *a*-C:H films. These films consist of carbon and hydrogen atoms, where the carbon atoms mainly form sp^2- and sp^3-hybridized bonds. Robertson proposed a tertiary diagram consisting of the sp^2, sp^3, and hydrogen contents to promote understanding of the *a*-C:H film structure [4–6]. Relationships between the mechanical properties and the structure of *a*-C:H films have often been discussed using this tertiary diagram. The mechanical properties of *a*-C:H films have been reported in many papers, and the relationship between the properties and film structure is now well understood [6,7].

On the other hand, some reports have indicated that *a*-C:H films have high chemical resistance [8,9], and it has been shown that *a*-C:H films can potentially be used as coatings for microfluidic devices [9]. In studies on the chemical resistance of such films, samples coated with an *a*-C:H film are usually dipped in a chemical solution, and cross sections of the dipped samples are observed using a scanning electron microscope. In these studies, the process used to evaluate the etching requires a long time and cannot be used to estimate the decrease in film thickness. Hence, the relationship between the chemical resistance of *a*-C:H films and the film structure has not been clarified. A quantitative method for evaluating the chemical resistance of *a*-C:H films in a short time is required. Sasaki et al. reported the etching rate of an *a*-C:H film by nitric acid solution using the phenomenon of surface plasmon resonance (SPR) [10]. The chemical resistance of an *a*-C:H film can be quantitatively estimated using their method. In this paper we report the structural dependence of the corrosion resistance of *a*-C:H films using this method.

SPR is the resonance between an evanescent wave on a metal surface and a surface plasmon wave [11–16], as shown in Fig. 1. At a thin metal film on a glass prism, light from a laser is irradiated from the glass, an evanescent wave penetrates through the metal film, and plasmon waves are also excited on the opposite side of the thin metal film [11–13]. When the wave numbers of the surface plasmon and

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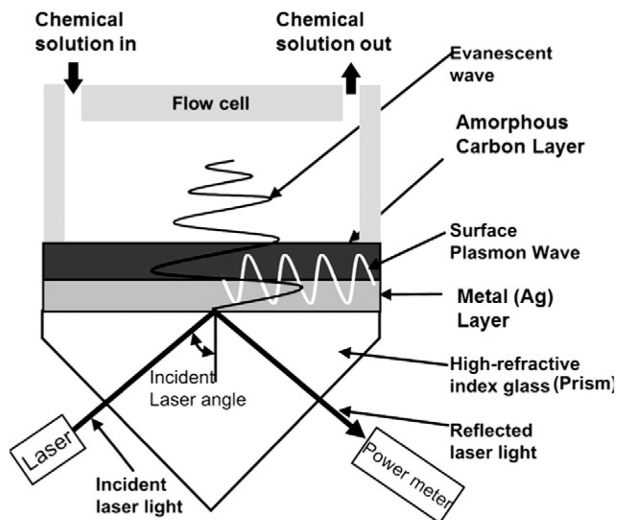

Fig. 1. Schematic illustration of SPR measurement device with the *a*-C:H multilayer structure and the flow cell.

evanescent waves are equal, SPR occurs. The SPR condition depends on the incident angle of the laser light because these waves depend on the incident angle of the laser light [16]. Under the SPR condition, the intensity of the reflected laser light from the back side of the thin metal film markedly decreases. The incident angle of the laser light under this condition is defined as the SPR angle (θ_{SPR}). The intensity of a plasmon wave depends on the refractive index of the metal surface. Hence, the refractive index changes with the configuration on the metal film surface, leading to a shift in θ_{SPR}. The area where this change in the refractive index can be detected is generally less than 200 nm above the metal film; this distance is mainly determined by the penetration distance of the evanescent wave [17]. The detection of a change on a metal surface such as a decrease in the *a*-C:H film thickness due to a chemical reaction is based on the concept of detecting a change in the refractive index. We have already reported the relationship between the film thickness on an Au layer and the shift in θ_{SPR}, and we proved its validity by comparing film thicknesses obtained by X-ray reflectivity and SPR measurements [18]. When a film with a thickness of nanometer order is deposited on a thin metal film, as shown in Fig. 1, a decrease in the film thickness due to a chemical reaction can be detected.

To investigate the structural dependence of the corrosion resistance of *a*-C:H films, three types of *a*-C:H films were deposited on metal surfaces. To clarify the sp^2/sp^3 ratio dependence, two non-hydrogenated amorphous carbon (*a*-C) films were deposited. To determine the effect of hydrogenation, an *a*-C:H film was also deposited on a metal layer. It is well known that graphite can react with nitric acid solution. Since an *a*-C:H film contains graphitic components, we chose nitric acid as the chemical reagent. We attempted to detect the decrease in the thickness of the *a*-C:H film due to the chemical reaction through the detection of SPR on the *a*-C:H/metal multilayer structure shown in Fig. 1. Furthermore, the rate of decrease in the thickness of the films due to the reaction with nitric acid was estimated using an SPR device with a multilayer structure.

2. Experimental method

Fig. 1 shows the multilayer structure used for SPR detection. S-TIH11 optical glass with dimensions of $25 \times 25 \times 1$ mm^3 and a refractive index of 1.778 was used as the substrate for the SPR device with the *a*-C:H/metal/glass structure. A silver (Ag) layer was prepared as the metal layer on the S-TIH11 glass by magnetron sputtering in argon gas using an Ag target (99.999%). *a*-C:H and *a*-C films were synthesized on Ag/S-TIH11 glass by two deposition methods. Two types of *a*-C films were synthesized using a filtered cathodic vacuum arc system (FCVA; Nanofilm Technology/Shimadzu DLC-200) with an integrated off-plane double bend (S-bend) [19]. Before deposition, the oxidation layer was removed by argon ion irradiation. The deposition chamber was evacuated to 10^{-4} Pa using a turbo molecular pump. A graphite target (99.999%) was used as the carbon source. Two *a*-C films were individually synthesized at substrate bias voltages of 100 and 400 V. In this paper, the samples deposited at these bias voltages of 100 and 400 V are denoted as "*a*-C 100 V" and "*a*-C 400 V", respectively. One *a*-C:H film was deposited by pulse plasma chemical vapor deposition (CVD) [20]. Before deposition, the oxidation layer was removed by argon ion irradiation. Acetylene gas with a flow rate of 20 cm^3/min was used as the carbon source. A pulsed bias voltage of −2.0 kV with a frequency of 14.4 kHz was applied to the substrate. This sample is denoted as "*a*-C:H CVD" in this paper. The deposition duration for each *a*-C and *a*-C:H film layer was controlled so that the film thickness was less than 100 nm, which is the limit of detection in SPR measurement [16]. To observe microstructural change, the amorphous carbon film deposited on a Si(100) substrate was conducted with an immersion test. In this

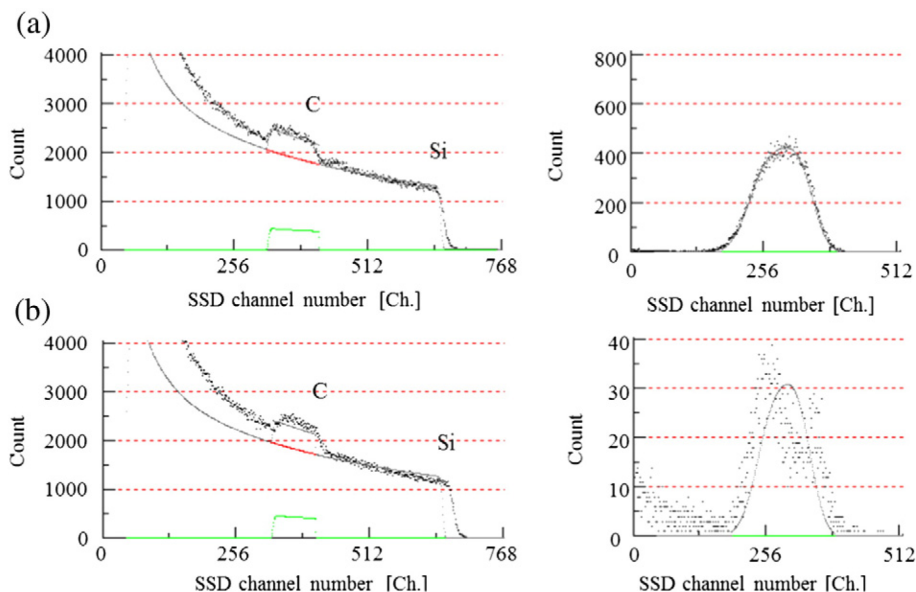

Fig. 2. RBS (left) and ERDA (right) spectra for *a*-C films deposited by FCVA (a) and *a*-C:H films deposited by CVD (b).

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