

Title	Laser PVD of Al ₂ O ₃ (Surface Processing)
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Citation	Transactions of JWRI. 19(1) P.113-P.118
Issue Date	1990-06
Text Version	publisher
URL	http://hdl.handle.net/11094/5859
DOI	
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Laser PVD of Al₂O₃

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Abstract

A fundamental investigation of Laser PVD (Physical Vapor Deposition) of alumina ceramics on nickel substrate was performed in broad ranges of substrate temperature and chamber pressure (vacuum degree) by using a cw Nd: YAG laser heat source. Amorphous alumina films were produced at a substrate temperature below 1000 K, above which films had Al₂O₃ crystalline structure. Deposition rates were 10 to 30 nm/s (0.6 to 2 μ m/min), which were considerably higher than those of other PVD processes. Exfoliation occurred at the substrate temperature of 600 K or lower and the chamber pressure of 5×10^{-2} Pa or higher. Cracks were present in the crystalline films after laser PVD at 1070 K, probably because larger thermal stress might be induced in the film during cooling from higher temperature due to a considerable difference in linear expansion coefficient between the film and the substrate. Films of 10 GPa (Hk = 1000) or harder could be obtained at more than 600 K in the chamber pressure range of 10^{-3} to 10^{-2} Pa (10^{-3} to 10^{-4} Torr), and a film of Hk = 40 GPa was produced at 1070 K and 6.5×10^{-3} Pa. The adhesive strength between the film and the substrate appeared to increase with a rise in the substrate temperature.

KEY WORDS : (Laser PVD) (YAG Laser) (Al₂O₃) (Ceramics) (Ceramic Coating)

1. Introduction

Recently "fine", "new" or "high-performance" ceramics have drawn many researchers' attention as new materials for the development of future industrial technology because of their good mechanical, thermal, chemical, electrical, magnetic and optical properties. Especially, ceramic coatings such as PVD (Physical Vapor Deposition), CVD (Chemical Vapor Deposition) and plasma spraying are expected to be practically significant processes because they can produce high quality materials from cheap substrates and make the best of materials by mutual good effects.

PVD processes have several advantages: 1) the use of poisonous reactive gases is not required, 2) bulk and/or powder ceramic materials can be employed as a target, and 3) generally the substrate temperature is relatively lower, in comparison with conventional CVD processes. A laser beam of high power/energy density can melt and evaporate materials, especially ceramics, easily in an extremely short time, and consequently laser PVD of ceramics is in the spotlight and has recently been studied.¹⁻⁸⁾ However, the conditions of the chamber pressure and substrate temperature were limited up to 1.3×10^{-2} Pa and below 800 K due to the ability of experimental apparatus, although harder films were produced

with a decrease in the pressure.⁸⁾

Therefore, in this study, the effects of chamber pressure and substrate temperature on the hardness, adhesive or fracture strength and structure of the film were investigated using a new laser PVD system which can cover a wider range of the PVD conditions.

2. Experimental Procedure

2.1 Laser PVD apparatus and conditions

Figure 1 shows a schematic set-up of the laser PVD process used in this investigation, and the experimental conditions are tabulated in Table 1.

A cw Nd: YAG laser beam (by The Laser Application Inc. Series 9500 CW Nd: YAG laser apparatus) is delivered into a vacuum chamber through the quartz window and protection glass and is focused on the target surface. The target is fixed on the holder, which has an inclination of 30° in that 1) the incident laser is irradiated on the surface effectively, 2) the absorption and/or scattering of the incident laser beam due to laser-induced plume/plasma and particles may be small, and 3) evaporated particles can fly up to the substrate efficiently and do not reach the window^{9,10)}. Alumina target was not heated at all by other heat sources in this experiment,

† Received on May 1, 1990

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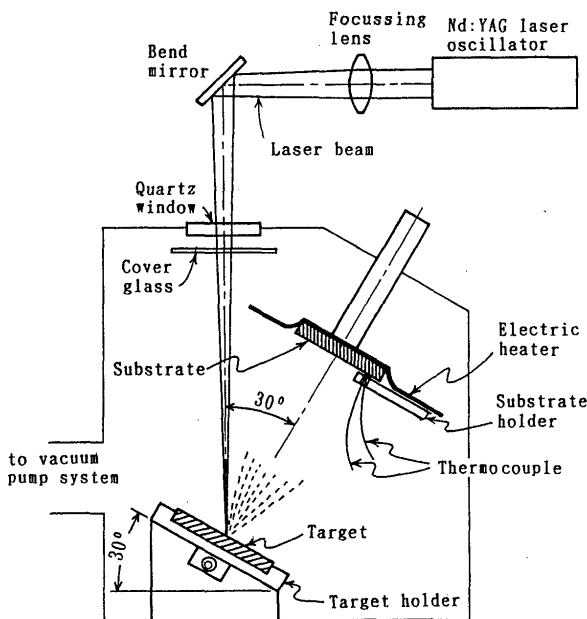
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Table 1 Laser PVD Conditions used

Laser power, P	: cw 85 W (on target)
Power density, P_d	: 5×10^3 W/mm ²
Target traveling velocity, v:	3.3 mm/s
Target material	: 99.5% Al ₂ O ₃
(Size)	65 ^t × 35 ^w × 2 ^t mm
Substrate	: Pure Nickel sheet
(Size)	20 ^t × 20 ^w × 2 ^t mm
Distance from Target to Substrate	: 65 mm
Substrate temperature, T	: 550 to 1070 K
Chamber pressure (Vacuum), P:	6.5×10^{-4} to 2 Pa

**Fig. 1** Schematic arrangement of cw Nd:YAG laser PVD process.

although preheating of ceramics is normally conducted to prevent or reduce thermal cracking. The holder can travel at a pre-set speed of 3.3mm/s (17mm/s maximum) in the maximum stroke range of 120mm (with 30mm width). A substrate can be heated up to 1070 K. The temperature of the substrate is monitored by a CA thermocouple inserted between the substrate and its holder. A vacuum pump system consisting of a rotary pump, a oil diffusion pump and a cryogenic panel can produce pressures below 1.3×10^{-4} Pa in the chamber.

A target and a substrate selected are alumina (Al₂O₃ of 99.5% in purity) sheet of 65 × 35 × 2mm in size and nickel sheet of 20 × 20 × 2mm in size. These materials are convenient because diffraction peaks from the film and substrate do not overlap each other in the X-ray diffractometer results.

2.2 Analytical procedure for film properties

The properties of laser PVD films were evaluated by various instruments and methods. 1) Film thickness and

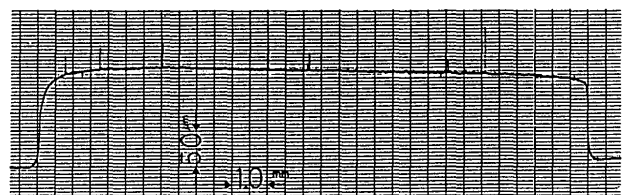
surface roughness were measured by surface profile and roughness measurement instrument. 2) Film hardness was measured at a load of 0.1N (= 10g, but sometimes 25 to 100g) for 20 sec by a knoop hardness tester. 3) Adhesive or fracture strength of the film was estimated with a scratch tester. A spherical diamond tip pressed on the film surface was linearly moved 5 mm while the press load was continuously increased from 0 to 20N. Cracking, flaking off and/or fracture of the film were detected by acoustic emission. 4) Film surface and fractured surface after the scratch testing were observed by SEM (scanning electron microscope), and EDX (energy dispersive X-ray spectrometer) was used to judge whether the fracture occurred between the film and substrate or in the film during scratch testing. 5) Crystal structure of the film was determined by X-ray diffractometer, and film compositions were measured by EPMA (electron probe micro-analysis) and AES (Auger electron spectroscopy).

3. Results and Discussion

3.1 Film thickness and deposition rate

Surface and cross sections of films were observed by OM (optical microscope) and SEM. PVD films were black at a pressure of 10^{-3} Pa, above which films were transparent at lower temperature but gray color appeared at more than 850 K. Examples of the PVD films will be shown below in SEM photos of Figs. 6 and 7, comparing the deposition and fractured surfaces and scratch test traces in the films as 550 and 1070 K in 6.5×10^{-3} Pa. Smooth surface films without any defect were produced, but the film appeared to be slightly rough at 1070 K.

Figure 2 indicates an example of surface profile of the film after laser PVD treatment for 20 min. The thickness of the film is approximately 10 to 15 μ m, and film roughness is about 0.5 μ mR_z, which is almost equivalent to the substrate roughness. From such results, the deposition rate was estimated to be about 10 to 30nm/s (0.6 to 2 μ m/min), which was very rapid in comparison with other PVD processes such as sputtering and ion plating.

**Fig. 2** Surface profile of PVD film.

3.2 Effects of PVD conditions on film hardness

Figure 3 shows the effect of chamber pressure on the film surface hardness at substrate temperatures of 620 and 870 K, which are a normally adopted temperature and a higher one, respectively. Films were harder at higher substrate temperature of 870 K than at 620 K, as compared at the same pressure. The hardest film, which was produced at 870 K and 6.5×10^{-3} Pa, had the hardness of $H_k = 20$ GPa corresponding to the hardness of sapphire or single crystal of Al_2O_3 . At both substrate temperatures the hardest films were yielded at a pressure of about 6.5×10^{-3} Pa. On the other hand, film hardnesses at a pressure of 6.5×10^{-4} Pa were approximately 0.5 to 1 GPa ($H_k < 100$). These are almost as soft as the hardness of metallic aluminum, and are abnormal, unbelievable,

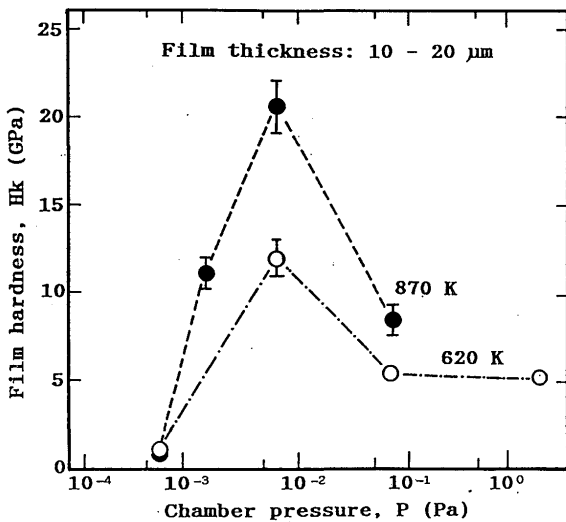


Fig. 3 Effect of chamber pressure on film surface hardness at substrate temperature of 620 and 870K.

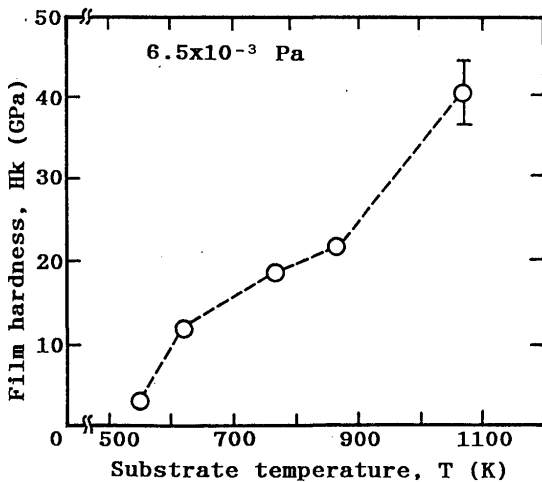


Fig. 4 Effect of substrate temperature on film surface hardness at chamber pressure of 6.5×10^{-3} Pa.

strange results. It is consequently concluded that there exists an optimum chamber pressure (vacuum degree) for the formation of hard films from Al_2O_3 targets.

Figure 4 indicates the effect of substrate temperature on the film hardness at a pressure of 6.5×10^{-3} Pa. The film hardness increased drastically according to an increase in the substrate temperature. At 1070 K, an extremely hard film of $H_k = 40$ GPa was made. This may be the hardest film that has ever been produced from Al_2O_3 target by laser PVD process.

Figure 5 shows a summary of the effects of chamber pressure and substrate temperature on the hardness of PVD film. The PVD conditions of the pressure and temperature to produce films of 10 GPa ($H_k = 1000$) or harder are indicated as a region. It is apparent that hard films are obtained at higher substrate temperatures in the pressure range of 10^{-3} to 10^{-2} Pa (10^{-5} to 10^{-4} Torr). The film hardness was softer at lower substrate temperature. As shown for reference, exfoliation took place at less than 600 K (lower temperature) and more than 5×10^{-2} Pa (higher pressure), and cracks occurred at 1070 K (higher temperature) and more than 10^{-3} Pa. Cracking is attributed to larger thermal stress induced in the film during cooling from higher temperature due to considerable difference of the expansion coefficients between the film and the substrate.

3.3 Fracture mode of film by scratch test

Films were subjected to the scratch test. Figure 6(a) and (b) exhibit the scratch test results (acoustic emission intensity during loading) and SEM photos of the film surfaces after the test of PVD films made at 550 and 1070 K, respectively, in 6.5×10^{-3} Pa. In the case of 550 K, the

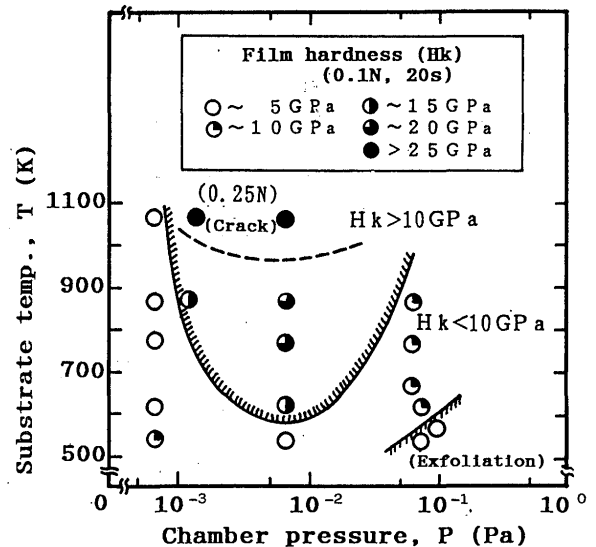


Fig. 5 Effects of chamber pressure and substrate temperature on film surface hardness, exfoliation and cracking.

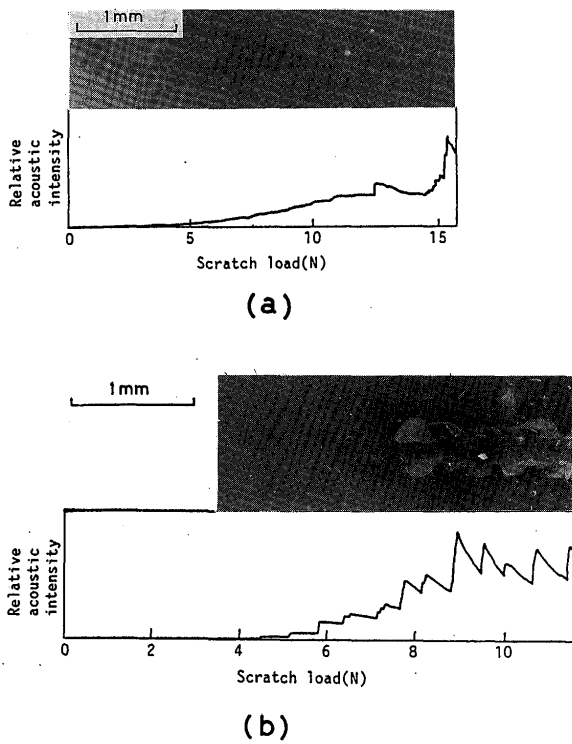


Fig. 6 Scratch test results of films produced at 550 and 1070 K under 6.5×10^{-3} Pa, showing acoustic emission intensity during loading and SEM photos of test traces on film surfaces.

film was depressed and became more and more concave and accordingly acoustic intensity increased gradually with an increase in the load. This is ascribed to the soft film of $H_k = 2.5$ GPa. The jump at the load of 12 N may show the adhesive strength of the film onto the Ni substrate. For the film at 1070 K, small cracks occurred in the film first and then the fracture (flaking or peeling-off) of the film took place at about 7.5 N.

Figure 7 shows SEM photos of fractured surfaces near the films made at 550 K (a) and 1070 K (b) after the scratch test and EDX results of the fractured surfaces (A, B) in contrast to EDX result of the film surface (c). EDX result in (c) indicates a high peak of Al element from alumina film and a small peak of Ni element from nickel substrate. In the case of 550 K in (a) and (d), a smooth fracture surface was observed, where Ni element only was detected. This suggests that the film was peeled off from the substrate. On the other hand, in (b) and (e), rough fracture surface was seen where Al element was chiefly obtained. This accounts for the fact that part of the film adheres to the substrate. It is therefore concluded that the fracture by the scratch test occurred between the film and the substrate in the film made at 550 K and in the film at 1070 K. Also, several high acoustic intensity signals in the scratch test of the films produced at a high temperature (of 1070 K) do not represent the "real" adhesive strength of the film to the substrate. It is

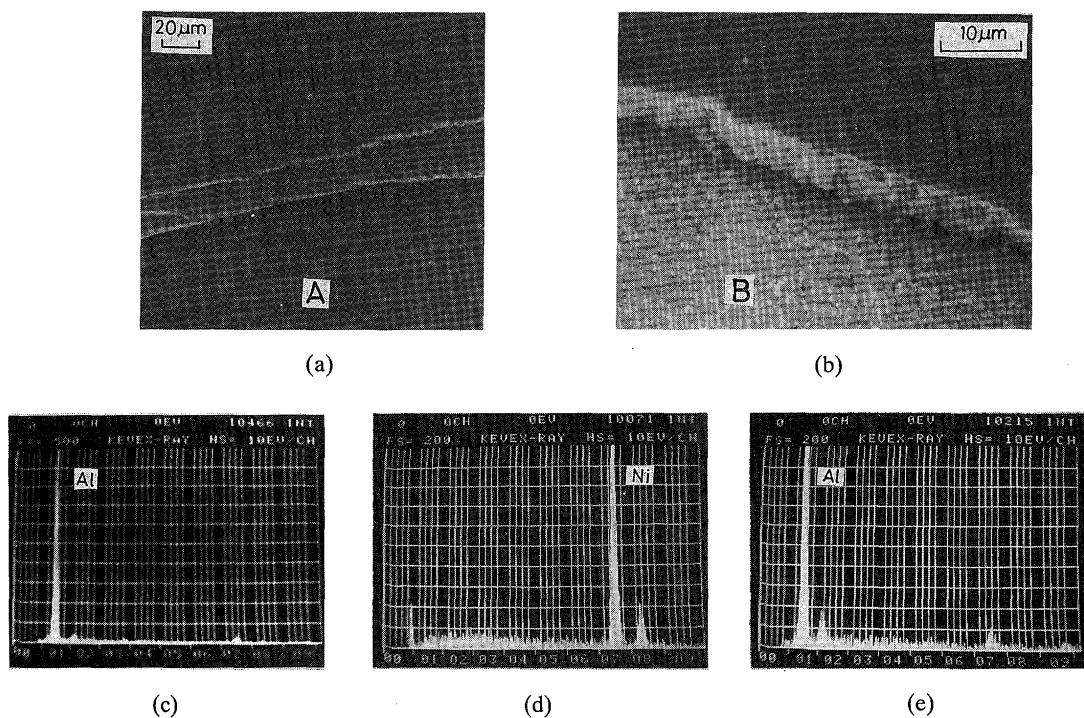


Fig. 7 SEM photos of fracture surfaces (after scratch test) of films made at 550 and 1070 K under 6.5×10^{-3} Pa, and EDX results from PVD film(a), and their respective fracture surfaces.

consequently suggested that adhesive strength of the film to the substrate should be higher with an increase in the substrate temperature, although further experiments should be performed.

3.4 Crystal structure and composition of film

Crystal structure of films were investigated by X-ray diffractometer. **Figure 8(a)** and (b) show X-ray diffraction results of the films at 550 and 1070 K, respectively. In (a), broad peak is observed at diffraction angles of 20 to 35°, and the film is amorphous. In contrast, as shown in Fig.8(b), the film prepared at 1070 K has a crystalline structure of γ -Al₂O₃.

From such results, it was found that γ -Al₂O₃ crystalline films were formed at 1070 K in the pressure of more than 10⁻³ Pa, and under other conditions (below 900 K) amorphous films were formed.

Compositions of films were investigated by EPMA and AES to especially elucidate why the films produced at 6.5 × 10⁻⁴ Pa were abnormally so soft as the hardness of aluminum alloys. EPMA results showed that the atomic weight percent ratios of Al-to-O in films produced at 6.5 × 10⁻³ and 6.5 × 10⁻⁴ Pa were both approximately 0.66, equal to the ratio of alumina; there was no distinct difference in Al-to-O ratio in the films between both

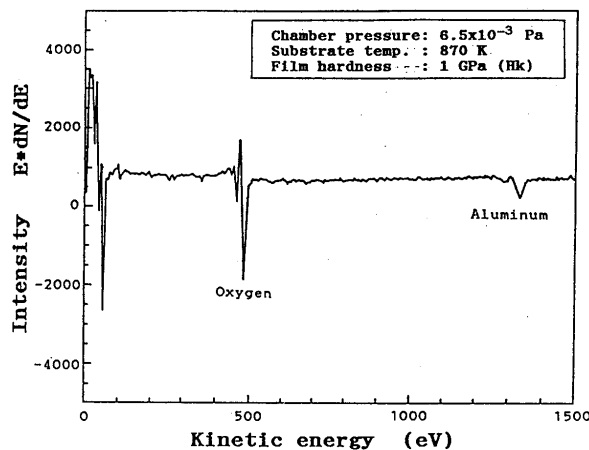
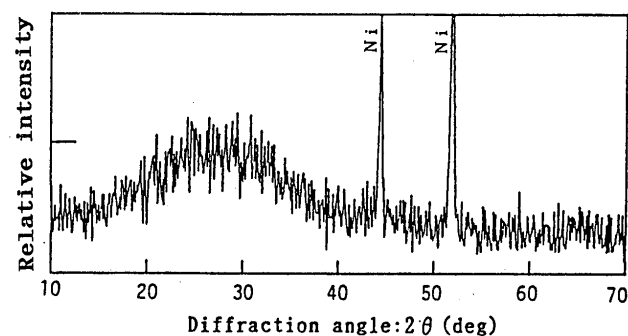
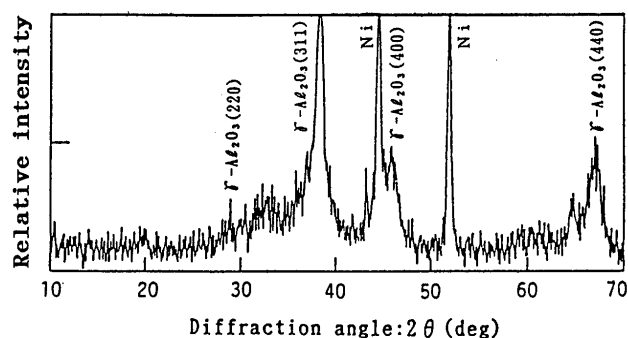


Fig. 9 AES result of film at 870 K and 6.5 × 10⁻⁴ Pa.

pressures. **Figure 9** indicates AES result of the film prepared at 870 K and 6.5 × 10⁻⁴ Pa. The existence of oxygen and aluminum elements is detected in the film. It was confirmed from these results that oxygen was contained in the film at 6.5 × 10⁻⁴ Pa as well as in any film made at higher pressure. The reason for the formation of soft films could not be interpreted in terms of the composition of the film. Further investigation will be needed in this regard.



(a)



(b)

Fig. 8 X-ray diffractometer results of films prepared at 550 K(a) and 1070 K(b) under 6.5 × 10⁻³ Pa.

4. Conclusions

A basic study of Nd:YAG laser PVD of alumina (Al₂O₃) ceramics to nickel substrate was conducted in wide ranges of chamber pressure (vacuum degree) and substrate temperature. Principal results obtained are as follows.

- (1) Deposition rates were 10 to 30 nm/s (0.6 to 2 μm/min), which were considerably greater than those of other PVD processes.
- (2) Amorphous alumina films were made at substrate temperatures of less than 1000 K. Above 1000 K the film possessed γ -Al₂O₃ crystalline structure.
- (3) Exfoliation occurred under the both conditions of lower substrate temperature (below 600 K) and higher chamber pressure (above 5 × 10⁻² Pa). It is understood that the adhesive strength of film is weak under such conditions.
- (4) In the case of crystalline hard films prepared at 1070 K, small cracks were present in the films, although the adhesive strength of the film to the substrate was judged to be high. These cracks may be induced by large thermal stress in the film because of a considerable difference in the expansion coefficient between the film and the substrate.
- (5) A hard film was produced by an optimum combined

conditions of chamber pressure and substrate temperature. In the pressure range of 10^{-3} to 10^{-2} Pa (10^{-5} to 10^{-4} Torr), 10 GPa (Hk=1000) or harder could be obtained above 600 K and a new record of the hardest Hk=40 GPa was established at 1070 K.

Acknowledgement

The authors wish to acknowledge Messrs. S. Hiramoto and M. Ohmine of Mitsubishi Electric Corp. for their co-operation of X-ray diffractometer and AES.

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