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Laser Physical Vapor Deposition of Si_3N_4 and SiC, and Film Formation Mechanism†

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Abstract

This paper describes the characteristics and formation mechanisms of laser physical vapor deposition (LPVD) films, which were produced on Ti or other metallic substrates from SiC or Si_3N_4 targets with a wide range of chamber pressures and substrate temperatures by using a cw Nd:YAG laser as a heat source for evaporation. Flat, smooth, dense, amorphous LPVD films with small particles were formed from any target. In the case of Si_3N_4 many crystalline Si_3N_4 particles of 1 to 15 μm size of globular or granular shapes and metallic Si particles of about 5 μm size of hemispherical shape were mainly observed in the films from porous high-purity and dense lower-purity targets, respectively. Such particles result from Si_3N_4 fractions or Si liquid ejected as spatter from the target. The N content in the amorphous film was reduced greatly in comparison with the original one in the target, probably because the laser-irradiated part of Si_3N_4 target was decomposed into Si and N, and N was easily pumped out as N_2 gas. Hard films of Hk=8~12 GPa were made from both Si_3N_4 targets at the substrate temperature of 723~923 K under the pressure of 0.02~1 Pa. In the case of SiC, small granular particles of less than 5 μm were seen in the film. Much harder SiC films of Hk=10~36 GPa were produced at 623~873 K under high vacuum of about 0.03 Pa. The scratch test showed an exfoliation load of more than 4 N for any substrate, and the fracture took place in the LPVD film on Ti, Ta and Type 304 substrates although the fracture occurred along the interface between the film and the substrate in the case of W. These suggest that the adhesion of the LPVD film was better in the former case than in the latter case. TEM observation of films or clusters formed on the Carbon film revealed that evaporated atoms might be deposited directly as a dense amorphous film under high vacuum of 0.01 Pa. On the other hand, at pressures of approximately 1 Pa or more, clusters or ultrafine particles must be at first formed on the substrate and then transformed into the film due to the thermal effect of the heated substrate.

KEY WORDS: (Laser PVD) (YAG Laser) (Ceramic Coating) (Film) (Surface Modification) (Clusters) (Ultrafine Particles)

1. Introduction

A laser with high power and high energy density, which can melt and evaporate any material easily, has been utilized as a heat source for the production of ultrafine high-performance particles[1,2] and hard or high performance laser PVD films[3-15]. Ceramics possess superior properties of high hardness, wear resistance, heat resistance, high performance, etc. In particular, laser PVD (LPVD) is receiving a considerable attention as a high-speed coating process for such ceramics[3,4,8-11]. Laser PVD has been performed using various ceramics of Al_2O_3, Si_3N_4, SiC, BN, Y-Ba-Cu-O, etc. as targets, and CO_2, YAG or Excimer lasers as the heat source[3-15]. These results showed that the N content was readily decreased compared with O or other elements[4,8-11,15], and that the ambient pressure and substrate temperature had a great influence on the hardness and adhesion of LPVD film[10,11]. An excimer laser PVD has been regarded as much slower deposition process than the other laser sources although better films may be generally formed[15]. Nevertheless, the effect of target purity on the properties of films has not been investigated, and few papers deal with the microstructural characteristics and formation mechanism of films.

In this study, therefore, LPVD was carried out by irradiating Si_3N_4 or SiC ceramic targets with a cw Nd:YAG laser with the objective of obtaining a fundamental knowledge of the production of crack-free, hard, adhered films. Two kinds of Si_3N_4 ceramic plates were used to reveal the effect of the purity or density of the target on film properties. The influences of LPVD

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parameters such as laser power, chamber pressure and substrate temperature on the properties and hardness of a film were investigated to establish LPVD conditions for the formation of a hard, dense film with good adhesion to the substrate. Microstructures and lattice structures of LPVD films, and compositional ratios of Si to N or C in the targets and films were examined by SEM, X-ray diffractometer and EPMA, respectively. The adhesion of a film to the substrate was evaluated by the Scratch test and the EPMA analyses of scratched traces after the test. TEM observation of evaporated particles was also performed to obtain a basic knowledge of formation mechanism of dense, amorphous LPVD films.

2. Materials and Experimental Procedure

A schematic representation of the laser PVD apparatus is shown in **Fig. 1**. A cw Nd:YAG laser beam of 40 to 170 W power is shot onto the target in a vacuum chamber through the quartz window and protection glass. The target is placed on the traveling holder with an inclination of 30°. The target holder is moved at the pre-set travel speed of 3.3 mm/s in a path of about 50 mm. The substrate is fixed on the other holder parallel to the target. The substrate is heated indirectly by a Mo resistance heater. The temperature of the substrate is monitored by CA thermocouples and is kept constant. A fair vacuum in the chamber can be achieved by a rotary pump, an oil diffusion pump and a cryogenic panel.

SiC and Si3N4 plates were used as targets, and were not heated by the other heat sources. Dense SiC of 99.5% high purity was employed, and two kinds of porous Si3N4 ($\rho \leq 2.15$) of 99.2% purity and dense Si3N4 ($\rho = 3.24$) of 92.0% purity were used to characterize the film properties, composition, etc. Ti was chiefly utilized as a substrate, although W, Ta, and Type 304 stainless steel, having different thermal linear expansion coefficients, were also used. The effects of the substrate temperature and chamber pressure on the hardness or adhesivity were examined using films produced in the ranges of 300 K to 873 K and about 0.01 Pa to 10 Pa. The distance between the target and the substrate of approximately 45 mm was selected on the basis of preliminary experiments.

3. Results and Discussion

3.1 Conditions of laser physical vapor deposition and characterization of LPVD film

LPVD films were produced under the conditions of plume formation. **Figure 2** indicates the formation conditions of plume induced from the SiC target as a function of laser power and defocused distance. Plume and LPVD film were formed within the higher power density conditions of higher power and shorter defocused distance (Pc and Pn). At laser powers of more than 60 W under the defocused conditions, the SiC target was broken in shatters and a poorly adhered film was produced (Pc). Therefore, a laser power of 60 W and the defocused distance of 0 mm (the focal point of a focusing lens) were utilized for the SiC target (within Pn).

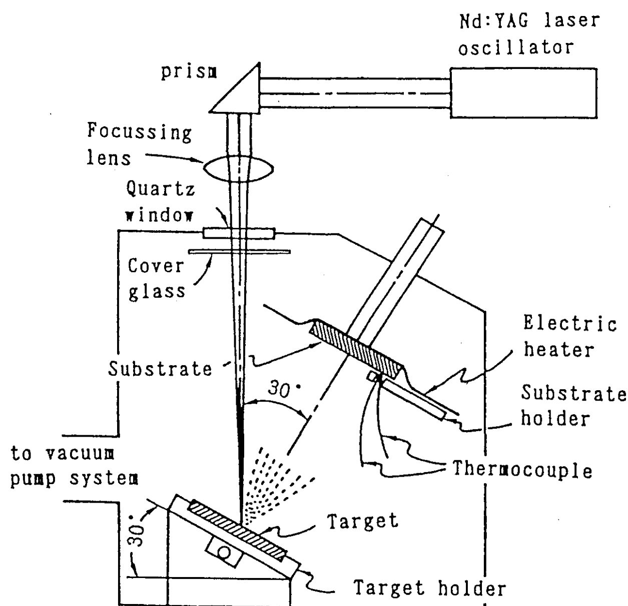


Fig. 1 Schematic of laser PVD apparatus.

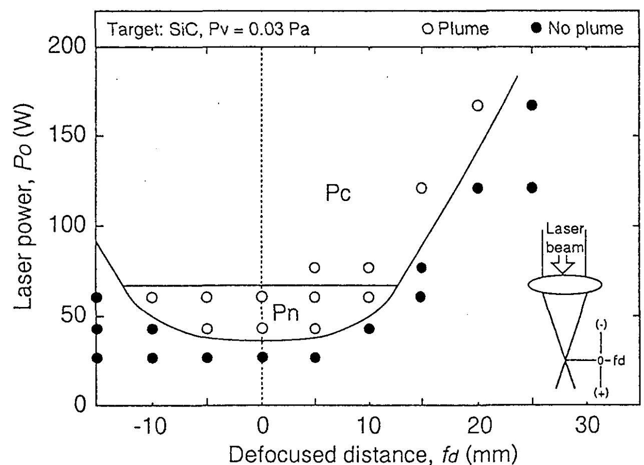


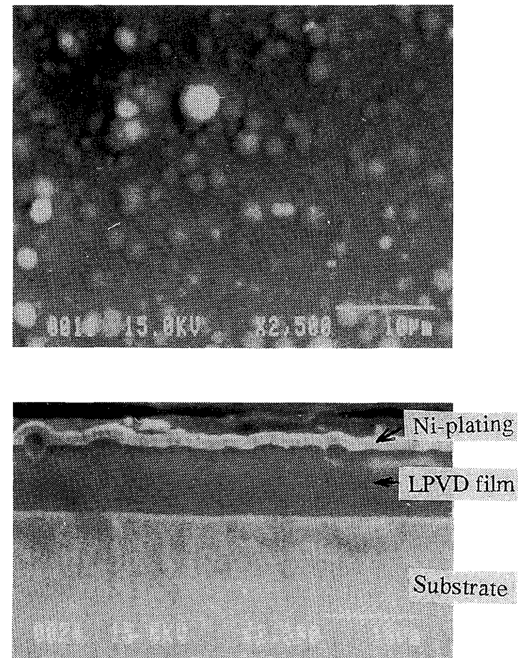
Fig. 2 Conditions of laser power and defocused distance for plume formation and cracking in SiC target.

In the case of Si3N4, grooves were formed on the target surfaces although the targets were resistant to cracking and shattering. The extent of grooving increased with an increase in the laser power, and then spattering occurred violently at higher powers, leading to the increase in the number of granular particles of μm size in the LPVD film. Therefore, low laser powers of 50 and 80 W were employed for porous and dense targets, respectively. There were optimum LPVD conditions for laser power, defocused distance and substrate temperature in producing crack-free films.

Figure 3 and **4** exhibit SEM photos of the surface and cross-sections of the LPVD film produced from SiC target, and the cross-sections of LPVD films made from Si3N4 targets. Nickel plating was applied to each film to prevent particles from dropping off the film during polishing of the cross sections. All LPVD films are composed of thin layer and small particles of a granular or hemispherical (semicircular) shape. It is revealed that particles or lumps on the surface are attributed to the existence of granular or hemispherical particles inside the film as well as on the film. It is especially noted that the shapes of particles are different between porous, high-purity Si3N4 and dense, low-purity Si3N4.

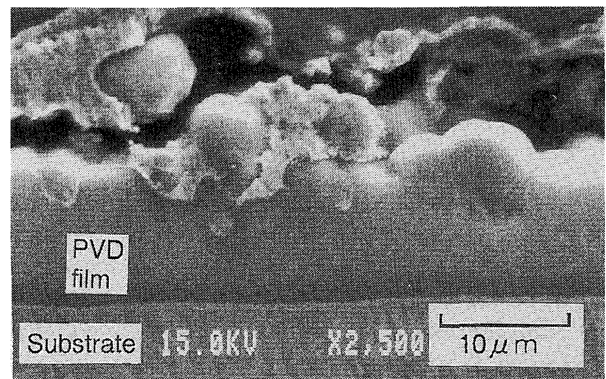
The compositions of the films were analyzed by EPMA. The analytical results of C and N contents in SiC and Si3N4 targets and films are shown in **Fig. 5**. The atomic ratio of Si vs. C in the SiC film was approximately 1:1. On the other hand, the N contents of the films were reduced to 30~40 at % from 57 at % of Si3N4 targets. These reduced contents are on the same levels with the film produced by an excimer laser[15]. The degree of N reduction was slightly smaller because of higher initial N content for high-purity target although the N reduction was hardly affected by laser power, chamber pressure and substrate temperature. Moreover, Q-mass analysis of evaporated particles confirmed that the reduction in N content might be caused by the extraction of N and N2 gas to the pump. In conclusion, the reduction in C or Si in the film is negligible for the SiC target, while N content is appreciably reduced in the film from Si3N4 targets.

Moreover, some granular particles had N contents of about 30 to 57% in the case of high purity Si3N4 target, whilst hemispherical particles from low purity Si3N4 target possessed high content of Si and a negligible content of N, and consequently were judged to be metallic Si. Based on the detailed observation of targets after LPVD, granular particles are judged to be the result of spatter from the porous target by thermal shock during laser-irradiation. On the other hand, it is supposed that dense Si3N4 target is decomposed into N and Si on the

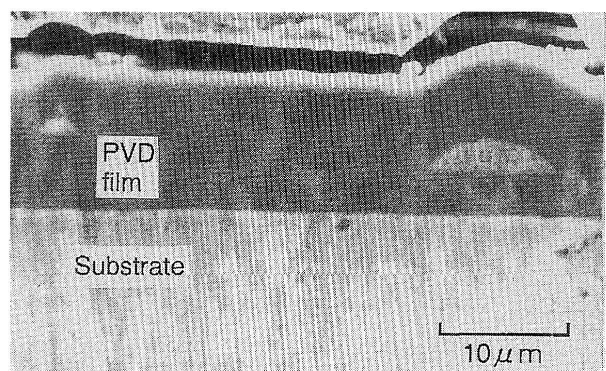


(b) Cross section

Fig. 3 SEM photos of surface and cross section of LPVD film produced from SiC target at P_v= 0.03 Pa, T_S=723 K, fd=0 mm and D_{ST}=40 mm.

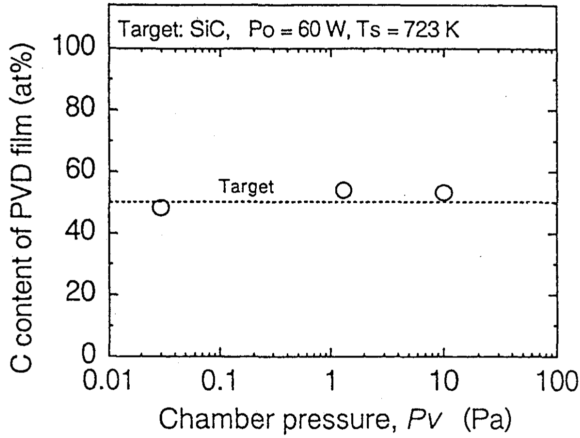


(a) 99.2% Si_3N_4 target (P_o=50 W, P_v=0.03 Pa)

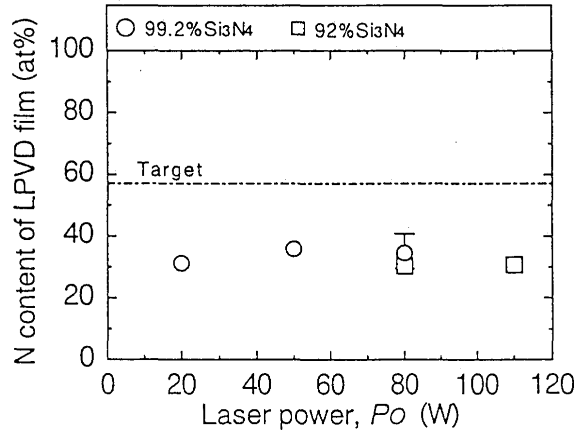


(b) 92.0% Si_3N_4 target (P_o=80 W, P_v=0.06 Pa)

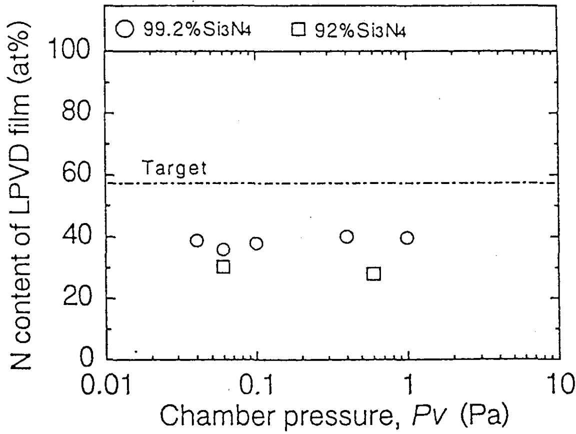
Fig. 4 SEM photos of cross sections of LPVD film made from Si3N4 targets.
(atT_s=723 K, fd=0 mm, $D_{S\text{-}T}$=45 mm)



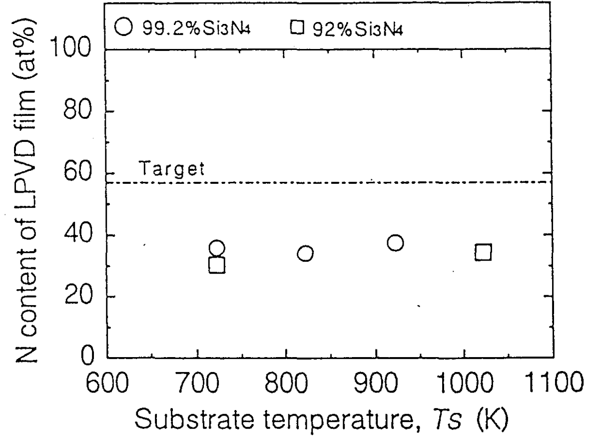
(a) SiC; Effect of pressure



(b) Si3N4; Effect of laser power



(c) Si3N4; Effect of pressure

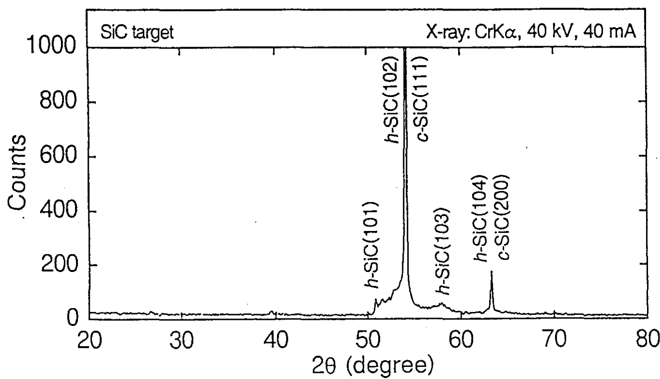


(d) Si3N4; Effect of substrate temperature

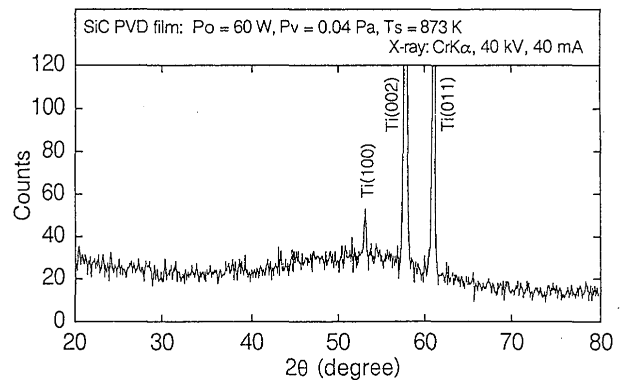
Fig. 5 C and N contents in films in comparison with those in SiC and Si_3N_4 targets.

laser-irradiated site, and molten Si residues are ejected as spatter from the target, and thereafter are impinged on the flat film, resulting in the formation of particles of the hemispherical shape.

Figure 6 and **7** indicate X-ray diffractometer results of 99.5% SiC and 99.2% Si_3N_4 targets and LPVD films made on Ti substrate from three kinds of targets. The structures of SiC and Si_3N_4 targets are c-SiC including

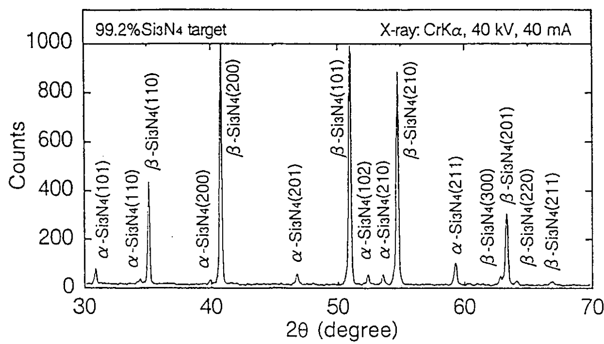


(a) SiC target

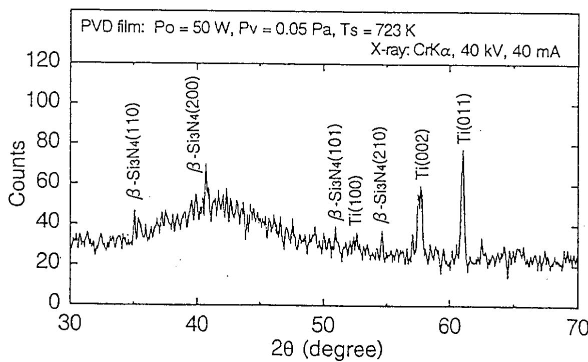


(b) Laser PVD film produced from SiC

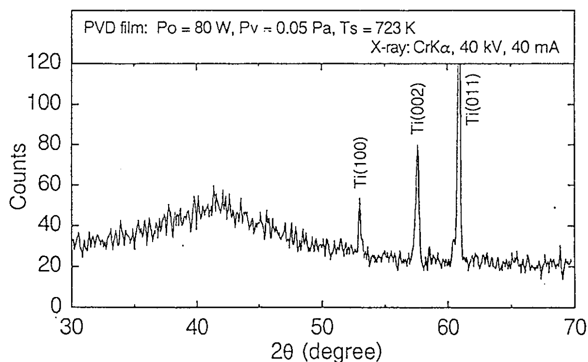
Fig. 6 X-ray diffractometer result of SiC target (a) and LPVD film produced on Ti substrate (b).



(a) 99.2% Si3N4 target



(b) LPVD film produced from 99.2% Si3N4 target



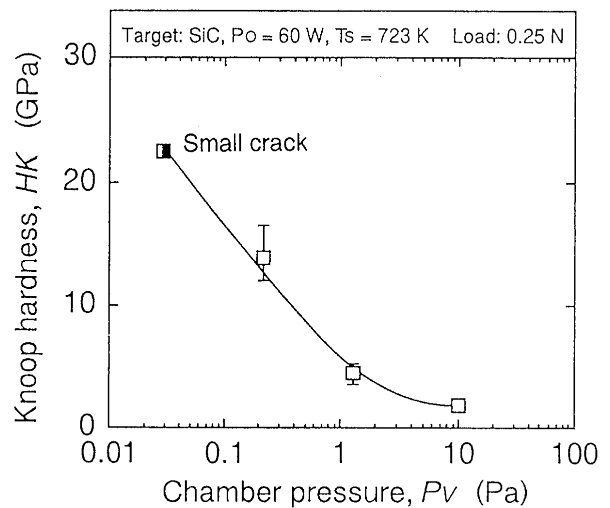
(c) LPVD film made from 92% Si3N4 target

Fig. 7 X-ray diffractometer result of Si3N4 target and LPVD films produced on Ti substrate.

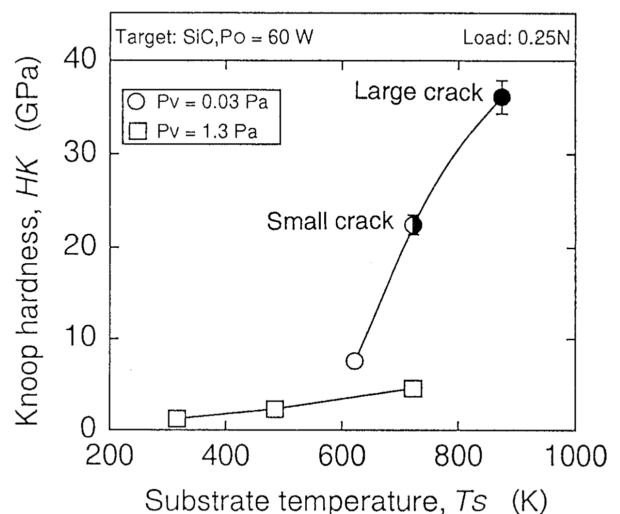
h-SiC, and β-Si3N4 including α-Si3N4, respectively. Their films are all judged to be amorphous in terms of broad diffraction patterns of $2\theta=40\sim70^{\circ}$ and $35\sim55^{\circ}$ in addition to high peaks from Ti substrates. In the case of the film produced from high-purity Si3N4 target, β-Si3N4 phase, which must come from particles, was identified in the LPVD film.

3.2 Hardness of LPVD films

Knoop hardnesses were measured on each film surface. **Figure** 8 (a) and (b) indicate results of Knoop hardnesses of films produced from SiC under various chamber pressures and substrate temperatures. The hardness of a film increases with a decrease in the chamber pressure and with a rise in the substrate temperature. The extremely high hardness of more than 30 GPa (3000 kgf/mm^2) was achieved at Ts=873 K. Cracks were formed in the films at hardnesses of more than 20 GPa. The increase in hardness with a decrease in the pressure may be attributed to the formation of a dense film. Hardening with a rise in the temperature is interpreted in terms of increased adhesion and higher compressive stresses induced in the film due to the difference of expansion coefficients between the film and the substrate[11].



(a) Effect of pressure



(b) Effect of temperature

Fig. 8 Effects of chamber pressure and substrate temperature on Knoop hardness of LPVD film surface produced from SiC target.

Figure 9 shows the surface hardnesses of LPVD SiC films produced on the substrates of W, Ta, Ti and Type 304 together with those of these substrates. Hard films of Hk>10GPa could be produced. The hardest film on the Ti substrate may be attributed to higher compressive stress, and the softest film on Type 304 is interpreted by considering stress relief due to severe cracks.

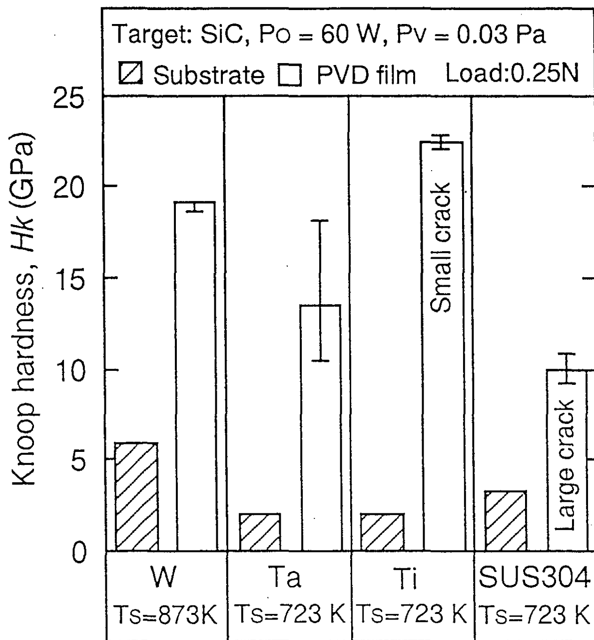


Fig. 9 Comparison of Knoop hardnesses of LPVD films on different substrates.

In the case of both Si3N4, hardnesses of LPVD films were about 8~12 GPa at the substrate temperature of 723~923 K under the pressure of 0.02~1 Pa. It was found that the hardnesses of films made from Si3N4 targets were lower than those of SiC films. The reason is considered to be due to the N reduction in the film and the existence of a larger number of particles.

3.3 Adhesion of LPVD film

The adhesion of LPVD film on the substrate was assessed by the Scratch test. **Figure 10** shows the trace on the film surface after the test and the acoustic emission intensity during loading, and thus the critical load for exfoliation of a film are compared among different substrate materials in **Fig. 11**. The critical loads for exfoliation were measured to be greater than 4 N on any substrate. **Figure 12** (a) and (b) exhibit SEM photos near the scratched traces and EPMA analysis results of the films and fractured areas on Ti and W substrates, respectively. C was detected from exfoliated surface on the Ti substrate, but not on the W substrate. These results signify that part of the LPVD film was existing on the scratched surface and the exfoliation or cracks happened in the film on the Ti substrate, while in the case of the W substrate the exfoliation took place along the interface between the film and the substrate. C was also detected on Ta and Type 304 substrates. A considerable content of N was analyzed on the scratched surface in Si3N4 targets as well. This suggests that Ti and Ta may be carbided and nitrided in the initial stages of LPVD, and the adhesion between the film and the substrate should be superior on Ta, Ti and Type 304 in comparison with W.

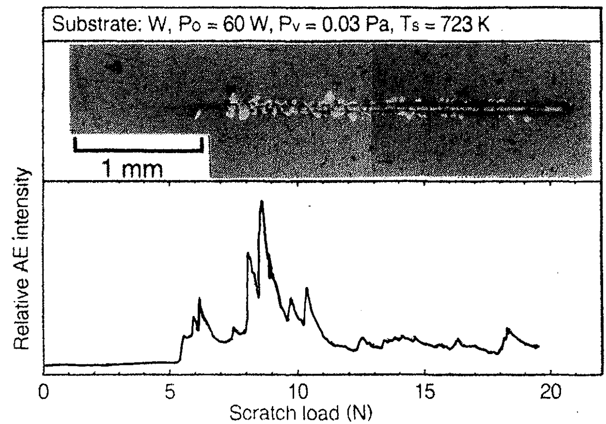


Fig. 10 Film surface subjected to Scratch test, and acoustic emission intensity during loading.

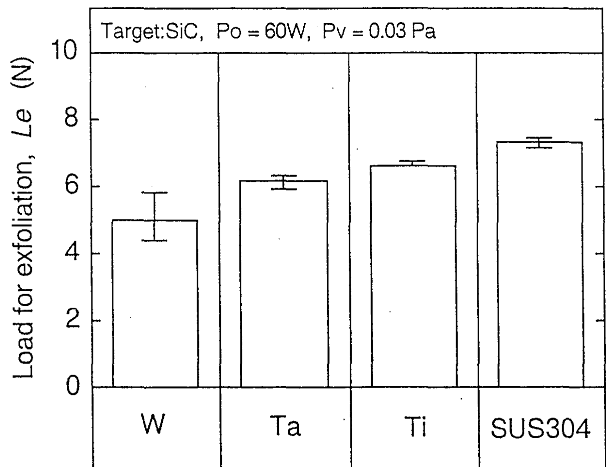
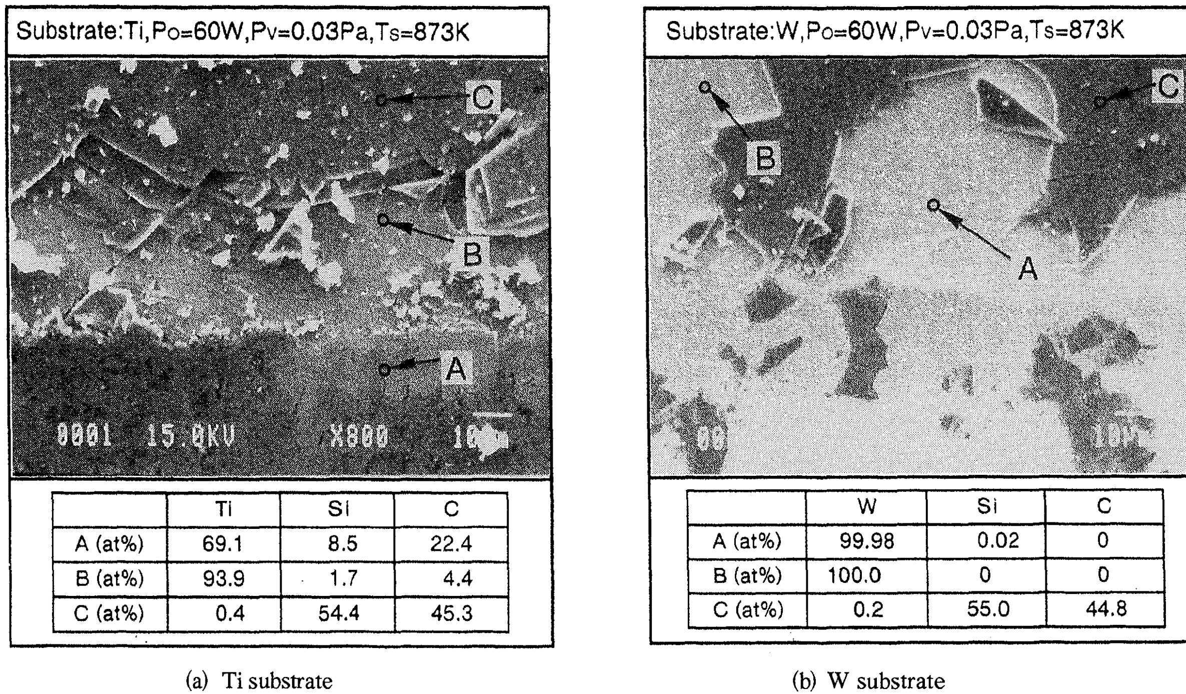


Fig. 11 Comparison of critical loads for film exfoliation among different metallic substrates.



	Ti	Si	C
A (at%)	69.1	8.5	22.4
B (at%)	93.9	1.7	4.4
C (at%)	0.4	54.4	45.3

(a) Ti substrate

	W	Si	C
A (at%)	99.98	0.02	0
B (at%)	100.0	0	0
C (at%)	0.2	55.0	44.8

(b) W substrate

Fig. 12 SEM photos near scratched traces and EPMA analyses of films and fractured areas on Ti and W substrates.

3.4 Mechanism of film formation

Evaporated particles or films deposited on the thin Carbon film, were observed by the TEM (transmission electron microscope) with the object of obtaining a better knowledge of film formation mechanism. **Figure 13** shows TEM photos of LPVD films made from SiC under the chamber pressure of about 0.01 to 10 Pa. The thin film is formed under the pressure of 0.013Pa. On the other hand, a great many groups of clusters of about 1 nm in size are seen with Pv=1.3 Pa. At Pv=10 Pa, a lot of ultrafine particles of 1 to 5 nm in size are observed. Similar films, clusters and ultrafine particles were also observed in the case of Si3N4 targets.

Consequently, it is considered that the formation of LPVD film is dependent upon the chamber pressure. The film should be formed by the deposition of atoms or ions because of the longer mean free path at extremely low pressure or high vacuum, while clusters or ultrafine particles are supposed to be produced before the film formation due to shorter mean free path of atoms under lower degrees of vacuum.

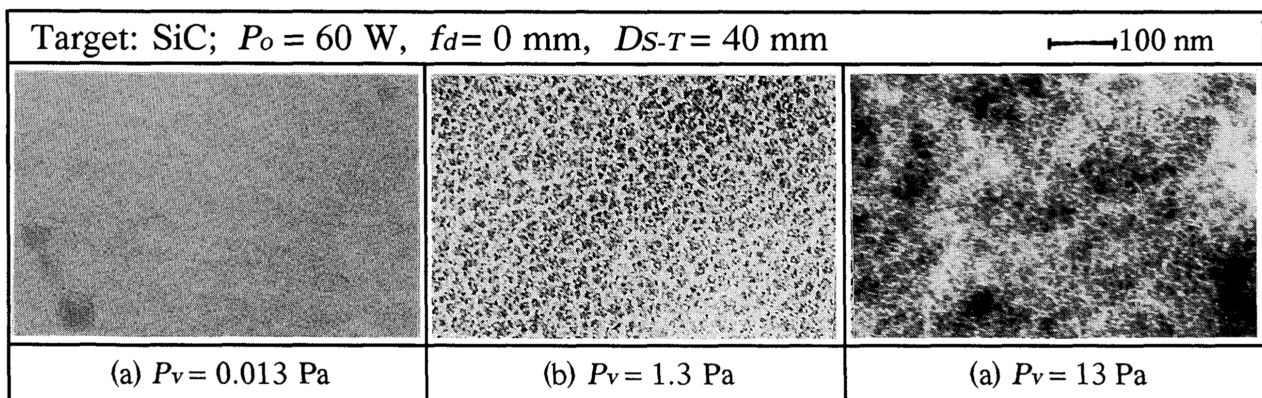


Fig. 13 TEM photos of film, clusters or ultrafine particles deposited and formed on carbon film after evaporation from SiC target at pressures of 0.013 Pa (a), 1.3 Pa (b) and 13 Pa (c).

Figure 14 also exhibits the TEM photos of the clusters made at Pv=1.3 Pa. It is clearly acknowledged that groups of clusters are transformed into a larger thin particles or films because of the action of electron irradiation energies during TEM observation. It is therefore concluded that active clusters or ultrafine particles could be transformed in the film by the effect of heated substrates at pressures of about 1 Pa or above. Thus such films may not be dense in contrast to those made under high vacuum, and the hardnesses of such films would not be so high.

It was revealed that the structures and properties of LPVD films were different depending on the kind, purity and density of target materials. **Figure 15** shows a schematic illustration of cross sections of LPVD films produced from SiC and Si_3N_4 targets. LPVD films are amorphous, including characteristic particles in them. Procedures to reduce or eliminate such particles are urgently required.

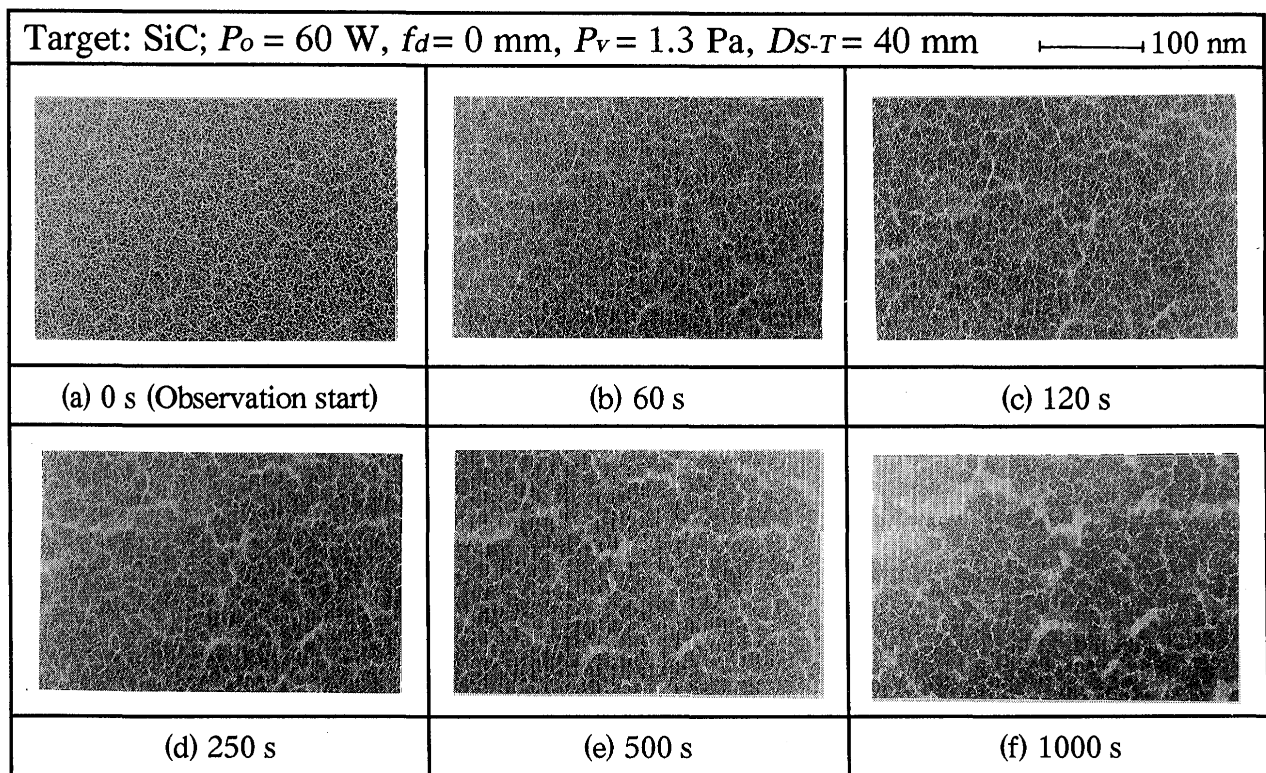


Fig. 14 TEM photos of clusters made at Pv=1.3 Pa, showing variation from clusters into flakes of films due to electron beam irradiation during observation.

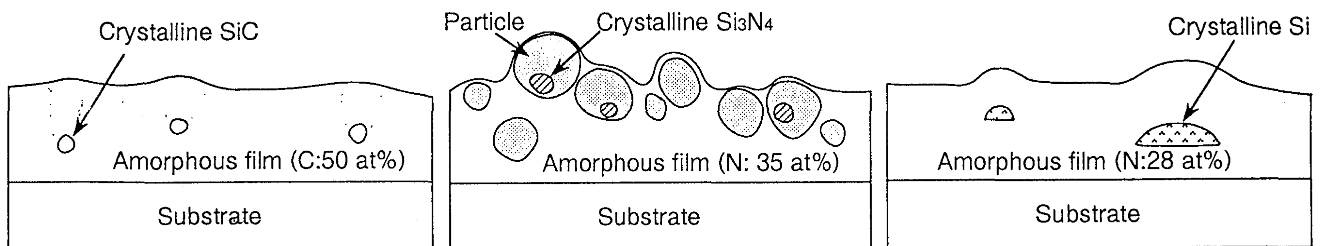


Fig. 15 Cross-sectional schematic of LPVD films produced from SiC and Si_3N_4 targets.

4. Conclusions

Ceramic coating of metallic substrates was performed by irradiating SiC and Si_3N_4 targets with a cw YAG laser. Principal results obtained were as follows:

(1) There were optimum LPVD conditions for laser power, defocused distance, chamber pressure and substrate temperature in forming better adhering, crack-free, hard films.

(2) LPVD film hardnesses were about Hk=8 to 12 GPa for Si_3N_4 targets under most conditions, while those of SiC films were increased up to Hk=20~30 GPa under the pressure to 0.01 Pa at the substrate temperature of 723~873 K.

(3) The structures of LPVD films made from SiC and Si_3N_4 targets were amorphous. The SiC film had the same compositions of Si and C as the target, while N content was reduced in the films made from Si_3N_4 targets.

(4) The film was composed of an amorphous layer plus small particles. The small particles must be fractions of SiC and Si_3N_4 targets and molten Si which are ejected as spatter and attached in hemispherical shape.

(5) Under the high vacuum of 0.01 Pa, an amorphous film is formed by the direct deposition of evaporated atoms due to longer mean free path.

(6) It is considered that clusters were at first formed but then transformed in the film due to the heating of the substrate under the low vacuum of more than 1 Pa.

(7) The Scratch test results showed that a load of more than 4 N was required for exfoliation on any substrate. Better adhesion was judged to be obtained on Ta, Ti and Type 304 substrates because the exfoliation took place in the film.

Acknowledgements

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