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Application of inductively coupled plasma to CVD and PVD

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Abstract

Inductively coupled plasma (ICP) can be successfully applied to lowering the process temperature of CVD and PVD without sacrificing the deposition rate and the film qualities. Application examples of ICP to CVD and PVD have been shown with films for wear and corrosion protection, such as TiN, CrN, DLC, C_xN_y, and Ti–B–N, for decoration, such as TiN and Cr, for flat panel display devices such as Al:ZnO, and for other functional purposes, such as TiO_2 and SnO_2. These films were prepared at a high deposition rate and at a low deposition temperature, and showed a high hardness and adhesion strength with a dense micro-structure, a good surface uniformity, a high crystallinity as well as superior electrical and optical properties.

Keywords: Inductively coupled plasma; CVD; PVD; Low temperature deposition

1. Introduction

The generation of high-density plasma is important for plasma assisted deposition, because high-density plasma can be used as an activation source for lowering the substrate temperature and enhancing the film quality. A higher plasma density will result in a higher degree of ionization of the metal atoms in the gaseous phase, which enables maximum control over the deposited films.

Several methods have been developed to obtain high-density plasma, such as ECR, Helicon and inductively coupled plasma (ICP). Among them ICP has the merit of easy implementation. ICP with an ion density of up to $10^{12}/cm^3$ can be produced simply by attaching an RF coil to an existing facility. Moreover, the scale-up problem for large area deposition can be also relatively easily solved.

In this paper some examples of applying ICP to the deposition of hard and wear resistant coatings, decorative coatings, and coatings for display devices and other functional purposes will be shown.

2. ICP generation and design

The mechanism of ICP generation is quite similar to the induction heating of conducting materials. In this case the plasma is the conducting material. Electrons gain energy through acceleration in an RF electric field, and the energetic electrons in turn ionize the gas atoms or molecules. In ICP, the discharge is sustained through the inductive coupling of RF power (typically 13.56 MHz, but also as low as 450 kHz) to the plasma from an antenna installed in the vacuum chamber. An immersed ICP antenna is driven by an 'L'-type tuning network and an RF generator.

Fig. 1 shows a design example of ICP assisted sputtering using various biasing schemes for the substrate, target and ICP antenna. The plasma parameters can also be changed by the antenna material and geometry. In the case of a simple metal antenna, where the antenna has direct contact with plasma, there is an additional capacitively coupled plasma contribution. As a result, a high plasma potential ($\geq$200 V) can be obtained. A dielectric shielded antenna can generate high-density plasma while keeping a lower plasma potential of less than several tens of volts. The number of turns of the coil, and its construction, can be also changed depending on the application and the experimental design. Early exper-

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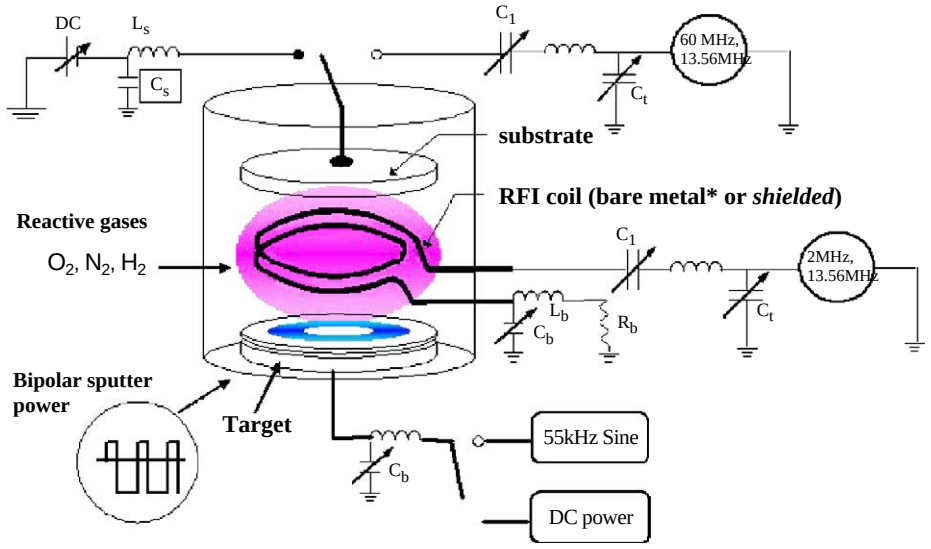


Fig. 1. Various biasing schemes for ICP magnetron sputtering.

imental work used RF coils with two or three turns and the coils were constructed of Cu tubing, which was water-cooled. Recent commercial tools have used a single-turn coil, which is not directly cooled.

3. Application of ICP to CVD

The high ion density in ICP enhances the reactivity of the precursor gases efficiently in the CVD chamber, and as a result, the deposition temperature can be significantly reduced without deteriorating the film qualities. Fig. 2 shows the deposition rate and the electrical resistivity of TiN, which was prepared by ICP assisted CVD at room temperature [1]. $TiCl_4$, N_2 and H_2 were used as the precursor, and the substrate was water-cooled. It should be noted that the deposition rate (>1 μm/h) was as high as could be obtained by PECVD at much higher process temperatures. The resistivity decrease indicates that the Cl concentration in the film decreased with increasing the ICP power. The TiN coating with a hardness of 2000 HK and a gold color may be applied to hard and decorative coating materials on plastic substrates. A high deposition rate (~300 Å/min) at a low temperature (300 °C) could be also achieved for SnO_2 production by ICP CVD [2]. SnO_2 films are used in a wide field of applications, e.g., gas sensors, heat mirrors, solar cells, and light emitting diodes. Well-crystallized SnO_2 films could be obtained with a high transmittance value in the visible light range (>80%), while the transmittance was as low as <40% in the mid infrared range (Fig. 3), showing an application possibility to heat mirrors. Diamond-like carbon (DLC) films deposited by ICP assisted CVD showed one of the highest hardness (37 GPa) values for DLC films produced by CVD [3]. The film hardness increased rapidly with decreasing hydrogen content in the film. By applying ICP, the hydrogen content could be reduced to approximately 20%, which is the lowest

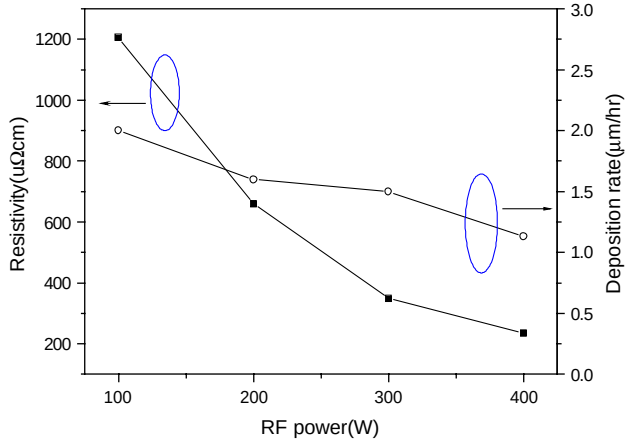


Fig. 2. Deposition rate and resistivity of the TiN films as a function of the RF power.

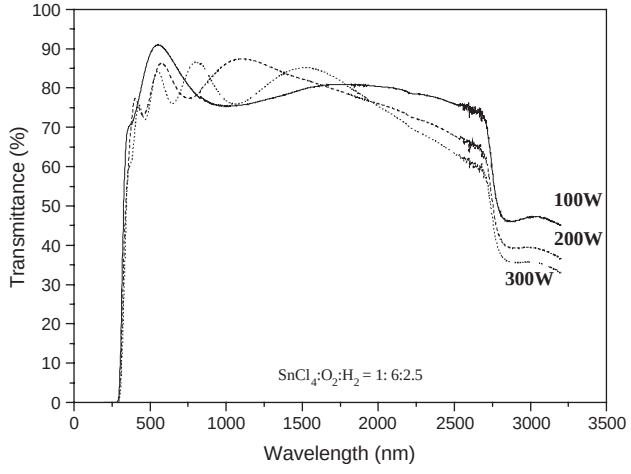
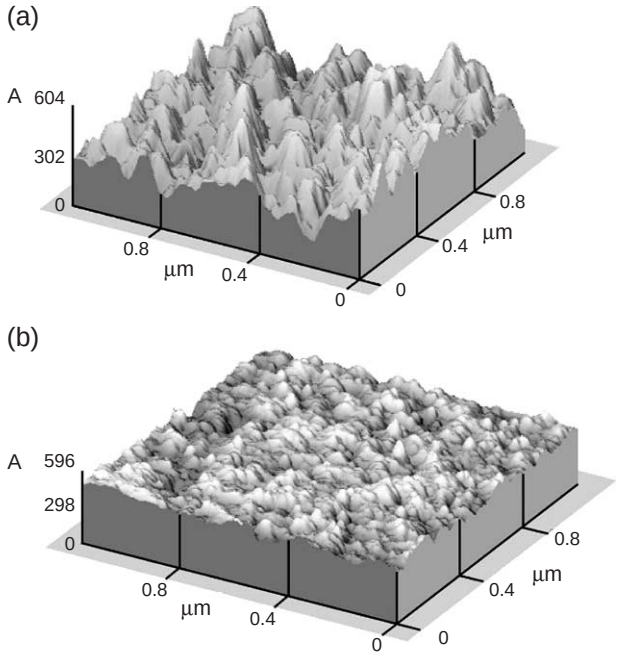


Fig. 3. Transmittance of the SnO_2 films using a UV/VIS/NIR spectrophotometer.

value among the reported ones obtained using other CVD methods, such as ECR CVD [4], PECVD [5], and even external type ICP CVD [6]. The hydrogen content was decreased with increasing bias voltage, which was also reported by Keudell et al. [7]. By applying ICP to CVD, carbon nitride films could also be obtained at a very high deposition rate [8]. By using a gas mixture of Ar, C_2H_2, and N_2, and with 200 W of ICP power, carbon nitride films with the hardness of 30 GPa were produced at a deposition rate of 6000 Å/hr, which was 2 or 3 times higher than those reported in the literature.

4. Application of ICP to PVD

The effect of a high ion density in ICP can be also found in films produced by PVD. Films with significantly high hardness and light transmittance, good surface uniformity, and a low impurity content as well as a high crystallinity could be produced with a high deposition rate and at low deposition temperatures. TiN films with a hardness as high as 65 GPa were obtained by ICP assisted sputtering [9]. The hardness increased with increasing ICP power up to 400 W at a substrate temperature of 300 °C. Despite the high hardness, the adhesion was high enough for industrial applications. TiN was also deposited on plastic substrates



Å	R_{p-v}	R_{rmsz}	R_{ave}
(a)	599	92.1	73.8
(b)	281	33.8	26.5

Fig. 4. Comparison of the roughness of the TiN coating between (a) UBM sputtering and (b) ICP sputtering (deposition on ABS substrate).

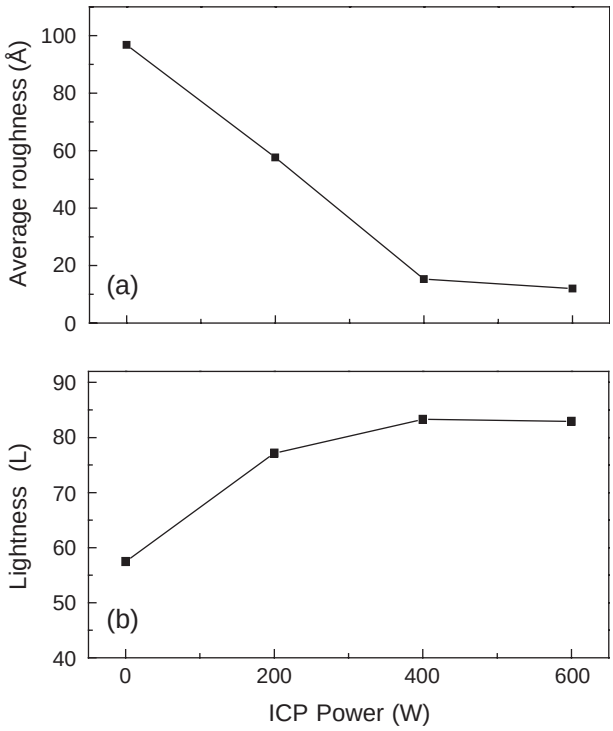


Fig. 5. (a) Average surface roughness and (b) surface lightness of the Cr coatings deposited with various ICP powers.

(Acronitrile–butadiene–styrene (ABS)) by ICP sputtering without extra substrate heating [10]. In order to suppress the plasma heating and re-sputtering effect, the ICP power was lowered to 200 W. The TiN showed a higher lightness and the color was more 'gold' like when compared with those of the TiN produced by conventional sputtering. The superior color property of the ICP TiN originates from the good surface uniformity and low impurity concentration. Fig. 4 shows that ICP TiN has a much better surface uniformity than the TiN film produced by UBM sputtering [10]. The high hardness and excellent surface uniformity are from the result of the small grain size of the film. Ti-B-N films prepared by ICP sputtering also showed very small grain sizes between 2 and 10 nm [11]. The hardness of the Ti–B–N film deposited at 400 W ICP and a −40 V DC bias voltage showed the highest hardness of 75 GPa. By applying ICP to sputtering, crystalline TiO_2 films with an anatase structure was obtained, even without additional substrate heating, while only amorphous TiO_2 films were produced at 160 °C without ICP [12]. In this case TiO_2 was produced by using a Ti target and supplying oxygen gas into the chamber. An insulated Cu antenna was used to generate the ICP in order to prevent the film contamination. TiO_2 is one of extensively studied coating materials owing to its wide rage application such as electronic devices, optical and hard coatings, photo catalysts, and antifogging and self-cleaning films etc. Anatase is known to have a higher photo catalytic activity than the other crystal types of TiO_2, due to its larger bandgap energy. The average transmittance of the films was approximately 80% in the visible light range and

no oxygen deficiency in the films could be found. Using reactive sputtering, Al doped ZnO (AZO) films could be produced also without intentional heating of the substrate [13]. By controlling the target voltage, the deposition process could be stabilized in the transition region without the typical hysteresis. The AZO films were deposited at various target voltages and the best film had a low electrical resistivity of 6.3×10^{-4} Ω cm and a high optical transmittance of 82% despite the low deposition temperature.

When the source material of the depositing film has a high evaporation rate, such as Cr and Zr, evaporation is the most efficient and economic vacuum deposition method for obtaining a high deposition rate. However, the low kinetic energy of the evaporated atoms results in columnar structured and highly porous coatings at high deposition rates. ICP can solve these problems under proper deposition conditions. Fig. 5 shows the roughness and lightness of Cr surface as a function of the ICP power [14]. Cr was evaporated by resistant heating, and deposited by using ICP without intentional substrate heating. The film brightness, which is important for decorative applications, is greatly affected by its surface roughness. At 400 and 600 W the surface roughness was quite low (~15 Å) and the coatings showed a mirror-like surface with a high brightness. The CrN coatings could be also produced by ICP evaporation without substrate heating, when nitrogen gas was added to the chamber. In this case, a bias voltage of −200 V was applied to the substrate to obtain a dense film structure. In the absence of the ICP power, CrN could not be formed at such a low substrate temperature. At an ICP power of 200 W both the Cr and Cr_2N phases were obtained. At 400 W, Cr and Cr_2N phases disappeared and only the CrN phase was found. Plasma has the effect of dissociating N_2, which can react with the evaporated Cr. Increasing the power enhances the dissociation rate, which increases the reaction rate with the evaporated Cr.

5. Summary

Inductively coupled plasma can be successfully applied to the deposition of hard and wear resistant coatings, decorative coatings, films for flat panel displays, and other functional materials using CVD and PVD. Using ICP, the deposition temperature can be lowered and still achieve a high deposition rate and without deteriorating the film properties. Application examples are shown with coatings such as TiN, CrN, C_xN_y, Ti–B–N, DLC, Cr, Al:ZnO, SnO_2, and TiO_2.

Acknowledgments

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References

[1] D.K. Lee, J.J. Lee, J.H. Joo, Surf. Coat. Technol. 171 (2003) 24.
[2] S.C. Hong, S.H. Lee, K.H. Nam, J.J. Lee, Thin Solid Films (2004) (personal communication).
[3] H. Kim, D.H. Jung, B. Pack, K.C. Yoo, J.J. Lee, Surf. Coat. Technol. 193 (2005) 255.
[4] N.A. Morrison, C. William, B. Racine, W.I. Milne, E. Martinez, J. Esteve, J.L. Andujar, Current Appl. Phys. 3 (2003) 433.
[5] J.K. Walters, C.D. Algar, T.M. Burke, J.S. Rigden, R.J. Newport, G. Bushnell-Wye, W.S. Howells, S. Sattel, M. Weiler, H. Ehrhardt, J. Non-Cryst. Solids 197 (1996) 41.
[6] D.J. Pappas, J. Hopwood, J. Vac. Sci. Technol., A, Vac. Surf. Films 12 (4) (1994) 1576.
[7] A.v. Keudell, T. Schwarz-Sellinger, W. Jacob, J. Appl. Phys. 89 (2001) 2979.
[8] D.K. Lee, D.H. Kang, H.Y. Lee, J.J. Lee, Surf. Coat. Technol. 193 (2005) 152.
[9] J.W. Lim, H.S. Park, T.H. Park, J.J. Lee, J.H. Joo, J. Vac. Sci. Technol., A, Vac. Surf. Films 18 (2) (2000) 524.
[10] H.D. Na, H.S. Park, D.H. Jung, G.R. Lee, J.H. Joo, J.J. Lee, Surf. Coat. Technol. 169–170 (2003) 41.
[11] D.H. Jung, H. Kim, G.R. Lee, B. Park, J.J. Lee, J.H. Joo, Surf. Coat. Technol. 174–175 (2003) 638.
[12] B. Park, D.H. Jung, G.R. Lee, J.J Lee, J.H. Joo, Surf. Coat. Technol. 174–175 (2003) 643.
[13] S.J. Jung, B.M. Koo, Y.H. Han, J.J. Lee, J.H. Joo, submitted to Surf. Coat. Technol.
[14] S.J. Jung, K.H. Lee, J.J. Lee, J.H. Joo, Surf. Coat. Technol. 169–170 (2003) 363.