ICP-CVD를 이용한 SnO₂ 박막 저온 증착 Low temperature preparation of SnO₂ films by ICP-CVD

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Abstract: Tin oxide films were successfully crystallized without additional heating by inductively coupled plasma assisted chemical vapor deposition (ICP-CVD). The degree of crystallization was affected by the ICP power, hydrogen flow and ion bombardment induced by negative substrate bias. The substrate temperature was increased only up to 150~180 °C by plasma heating, which suggests that the formation of SnO₂ crystalswas caused by enhanced reactivity of precursors in high density plasma. The hardness of deposited tin oxide films ranged from 5.5 to 11GPa at different hydrogen flow rates.

1. Introduction

Tin oxide (SnO₂₎ films are intensively studied owing to its wide range applications such as gas sensors, solar cells, electroluminescent displays, and light emitting diodes. Moreover, SnO₂ has better mechanical properties, e.g., higher hardness, chemical stability and abrasion resistance than other Transparent Conductive Oxides (TCO) [1], which are important for application to the TCO films on polymers. However, for the deposition of SnO₂ on polymer substrates, the process temperature should be lower that the glass transition temperature of the polymers (polycarbonate(PC) <150 °C and polyether sulfone (PES) < 200 °C). According to the reports in the literature, SnO₂ films can be synthesized at >500 **c**C by conventional chemical vapor deposition (CVD). Although plasma is used to CVD, the process temperature (>300 **C**C) is still too high for the deposition of SnO₂ on polymer substrates. In this work, it was tried to synthesize SnO₂ films at a much lower temperature by applying inductively coupled plasma (ICP) to CVD, and the properties of the film was investigated. ICP has been successfully applied to low temperature deposition of many coating materials without deteriorating the film qualities [2].

2. Main subject

SnO₂ films could be synthesized without external heating by ICP assisted CVD. The film grown at a low ICP power showed an amorphous structure, while well crystallized films were produced at higher ICP powers. It was also found from the XRD results that the hydrogen flow rate is also an important process parameter for the crystallization.

In order to find out the effect of plasma heating on the crystallization of the coating, the substrate temperature was measured during the deposition. For the measurement, an electrically insulated thermocouple was directly embedded in a 1mm thick PES substrate. At the ICP power of 300W, substrate temperature rose up to 180°C, while at 200W it was only increased to 150°C. Since SnO₂ crystallizes at >500°C in thermal CVD, the plasma heating cannot be the main reason for the crystallized SnO₂ film formation.

The plasma density was determined by a Langmuir probe at the point 1cm above the substrate. The plasma density increased significantly between 100 and 200W of the ICP power as shown in Fig. 3. It is well known that the capacitively coupled E mode transferred to the inductively coupled H mode in ICP. Owing to the efficient power transfer to the discharge at higher ICP powers, precursors in plasma could be easily dissociated or ionized. The plasma density was also increased with increasing the hydrogen flow rate, which might explain the XRD result (Fig. 1(b)). The rf bias voltage also affected the XRD peak intensity by controlling the ion energy. The optimum rf bias voltage was -20V at 10sccm hydrogen flow rate, while it was -60V in the absence of hydrogen.

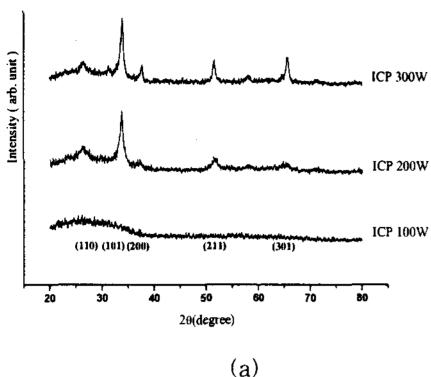
The microhardness of deposited SnO₂ films ranged between 5.5 and 11GPa at different hydrogen flow rates. The contact angle of SnO₂ film is lowered from 30 to 0 degree as increasing ICP power.

3. 결 론

Crystallized SnO₂ films could be deposited with no additional heating using ICP assisted CVD. The crystallization of tin oxide films was formed at the condition of >200W ICP power and >10sccm hydrogen flow rate. The plasma heating during experiment is only up to 150~180°C. This low temperature crystallization is supposed to be related to the plasma density near substrate corresponding with XRD results. The plasma density to decide crystallization was supposed to exist a specific value, between 1×10¹⁰/cm³ and 4×10¹⁰/cm³ in our system. The micro-hardness of tin oxide varies from 5.5 to 11GPa at different hydrogen flow rates. The contact angle of SnO₂ film is lowered from 30 to 0 degree as increasing ICP power.

참고문헌

- [1] Te-Hua Fang and Win-jin Chang, "nanomechanical characteristics of SnO₂:F thin films deposited by chemical vapor deposition", Applied surface science. 252, 1863 (2005).
- [2] J. J. Lee, "Application to inductively coupled plasma to CVD and PVD", Surf. Coat. Technol. 31, 200 (2005)



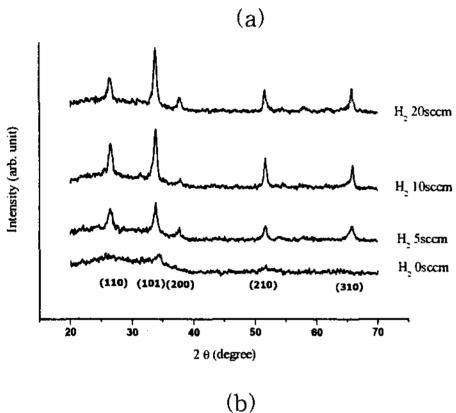


Fig. 1 XRD patterns of SnO₂ films deposited at different (a) ICP powers, and (b) H₂ flow rates

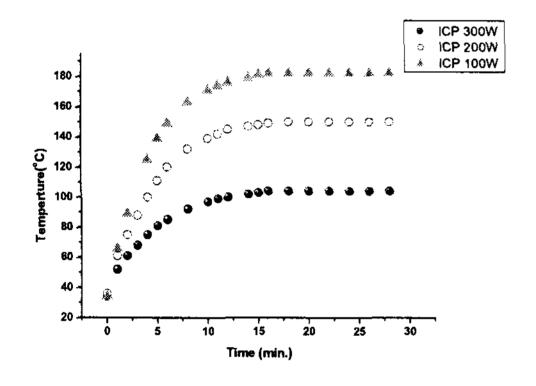
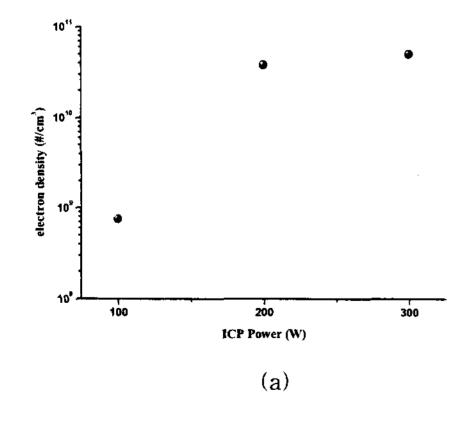


Fig. 2 Substrate temperature induced by plasma heating with varying ICP power



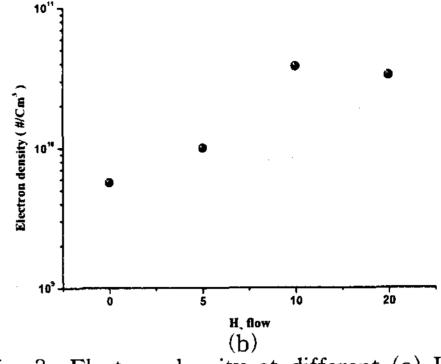


Fig. 3 Electron density at different (a) ICP powers and (b) H₂ flow rates.

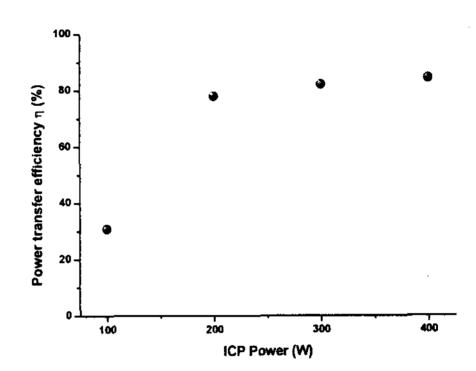


Fig. 4 The value of power transfer efficiency at a different power

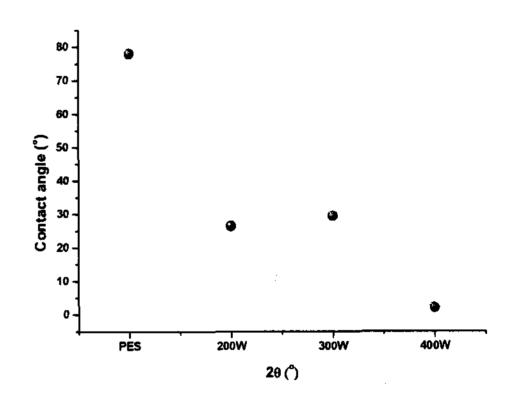


Fig. 5 Micro-hardness characteristic of SnO₂ films at a load time of 10s, the applied load 4mN as a function of H₂ flow rate.

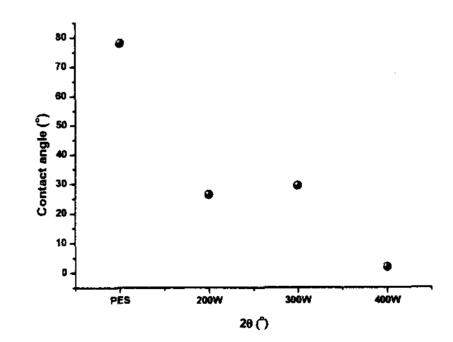


Fig. 6 Contact angles of SnO_2/PES films deposited at a different power