Real-time Spectroscopic Ellipsometry Studies of the Effect of Preparation Parameters on the Coalescence Characteristics of Microwave-PECVD Diamond Films

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Abstract

The growth of diamond films in plasma enhanced chemical vapor deposition (PECVD) processes requires high substrate temperatures and gas pressures, as well as high-power excitation of the gas source. Thus determining the substrate temperature in this severe environment is a challenge. The issue is a critical one since substrate temperature is a key parameter for understanding and optimizing diamond film growth. The precise Si substrate temperature calibration based on rapid-scanning spectroscopic ellipsometry have been developed and utilized. Using the true temperature of the top 200 Å of the Si substrate under diamond growth conditions, real time spectroellipsometry (RTSE) has been performed during the nucleation and growth of nanocrystalline thin films prepared by PECVD. RTSE shows that a significant volume fraction of nondiamond (or sp^2-bonded) carbon forms during thin film coalescence and is trapped near the substrate interface between ~300 Å diamond nuclei.

1. Introduction

As the applications of diamond thin films become more demanding, real-time monitoring of the deposition process becomes increasingly important for the improved fine tuning and control of the process [1]. Optical probes are advantageous because they are passive and require no equipment internal to the reactor. RTSE is among the most powerful optical probes available. Among the important parameters in diamond film deposition, the temperature is the most difficult to determine and control over the required range (typically 400~1000 ℃). the origin of the problem is the extreme

environment associated with diamond film deposition. This includes not only the high substrate temperature, but also the high power flux at the substrate surface due to the impinging particles and the radiation used for gas excitation. After the temperature calibration, this result is used in the experiments for the diamond thin film growth. RTSE measurements can provide the time evolution of the bulk and surface roughness layer thicknesses, as well as the time evolution of the volume fractions of the different components in the bulk layer. Such results are obtained from an analysis of data collected during the film growth.

2. Experimental Procedures

Untreated Si wafer substrates are used for substrate temperature calibration. Substrates are mounted onto the graphite substrate platform which is rf heated to a temperature that can be controlled independently of the microwave power over a relatively wide range. With the system well aligned and calibrated, the temperature is increased to the maximum accessible nominal value as indicated by a thermocouple embedded in the substrate holder. After measurement, the thermocouple temperature is reduced to another value and the measurement is repeated. These procedures are repeated in the temperature calibration experiments with and without H_2 plasma. The deposition system and RTSE instrumentation used to investigate the diamond growth process are the same as those used in the temperature calibration experiments. However, in this case, dry substrate seeding is used. In this seeding procedure, the crystalline Si (c-Si) wafer substrate is hand polished with <0.25 ㎛ diamond powder. A cotton swab is used to abrade the substrate in a circular pattern, and then the residual powder on the surface is removed with a clean cotton swab. With the exception of the polishing procedure, the detailed methods for this experiment follow those of the temperature calibration experiment.

Data analysis employs the Bruggemann effective medium approximation (EMA), multilayer optical computation and least regression analysis(LRA) to extract photon energy-independent free parameters of thickness and material volume fraction [2]. The EMA is used to determine the dielectric function of composite materials [e.g. (diamond) + (sp^2 C) + (void)] from the dielectric function of the components and their volume fraction.

3. Results and Discussions

The results(Fig. 2) extracted from the typical experimental data for a critical point analysis shown in Fig. 1 show clear trends. In the absence of a plasma at 1Torr pressure, the thermocouple reads too high by values ranging from 30 ℃ to 140 ℃ for 200 ℃<T_{ellips}<750 ℃. For a plasma power of 1000 W, the thermocouple reads too low by values ranging from 100 ℃ to 15 ℃ for 350 ℃<T_{ellips}<900 ℃. Fig. 3 provides an overview of the fixed and variable parameters in the LRA that characterize the microstructural evolution of the diamond film. In the initial stage of growth, the film ids expected to exhibit isolated diamond nuclei that increase in size with time. With continued growth, the diamond particles make contact and interlock to form a continuous film. The surface layer simulates roughness, and its sp^2 C and void contents simulate the defects in the protruding grains and the free space component between the protrusions, respectively. The underlying layer simulates the interlocking grains of the bulk layer, and the sp^2 C content simulates the graphite defects in the grains at grain boundaries. The void content simulates trapped space resulting from incomplete interlocking of nuclei.

4. Conclusion

Two applications of interest were described. First, the calibration of Si wafer substrate temperature under the conditions of diamond growth was described. Second, the evolution of the microstructure and absorbing sp^2 C carbon content in nanocrystalline diamond prepared under conditions that lead to optical quality films was described. The results provide insights into diamond deposition that may lead to improvements in the ultimate quality of the amterials.

It is found that the real-time SE data are consistent with a transition from a one-layer optical model, describing isolated particles, to a two-layer model, describing a coalesced structure. Overall it is found that isolated diamond nuclei prior to contact exhibit a low volume fraction of sp^2 carbon (typically about 0.01~0.02). When the particles make contact, a zone with a high volume fraction of sp^2 C defects is formed. Even under optimum conditions, these defects are trapped between coalescing crystallites, where insufficient H exposure prevents them from being eliminated in the subsequent growth process. However, once the film surface becomes smooth, optimum conditions impede further sp^2 C formation.

References

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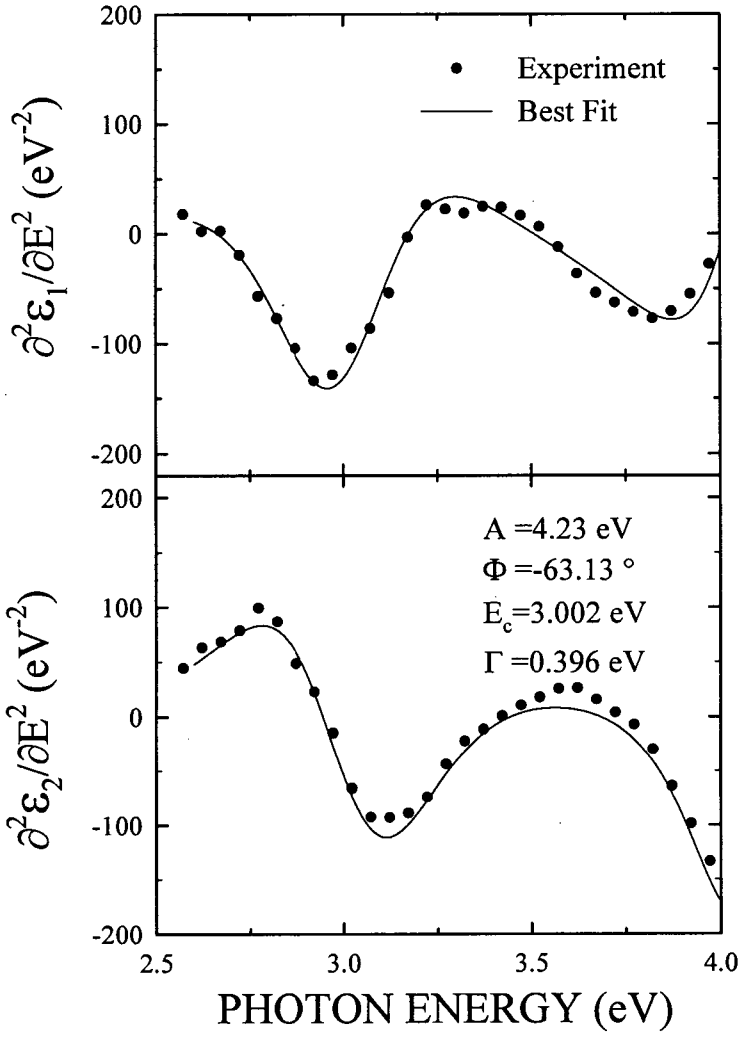

Fig. 1. Critical point analysis used to determine the amplitude(A), transition energy(E_c), phase factor(Φ), and broadening parameter(Γ) from the E_1 transitions in single crystal Si substrate.

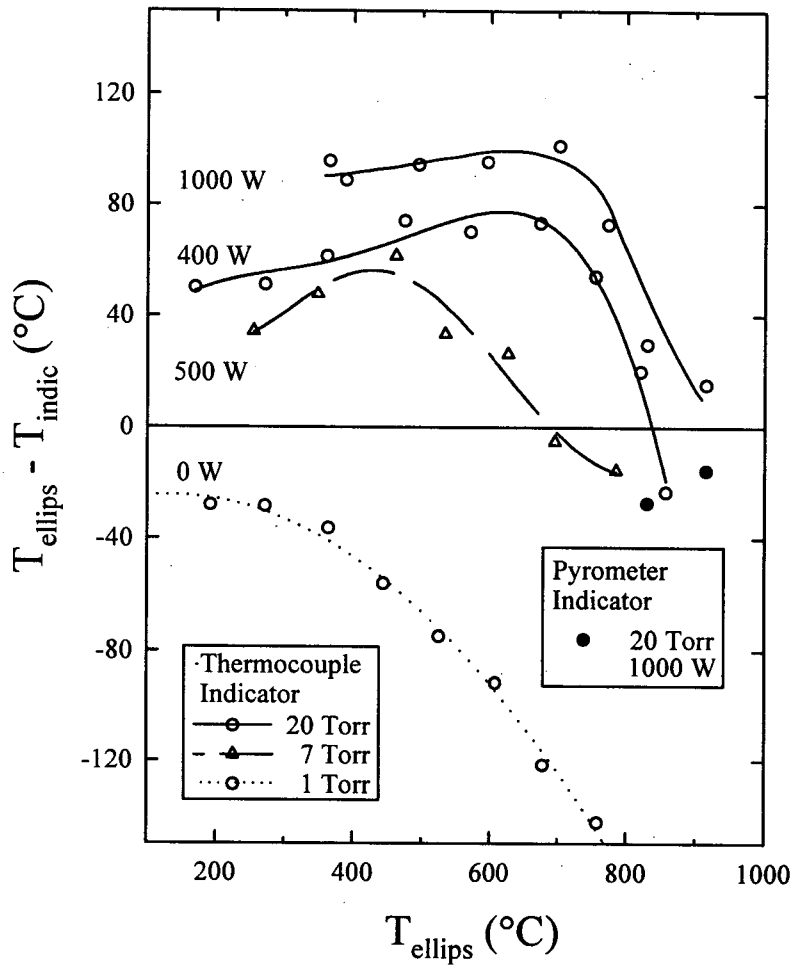

Fig. 2. The difference between the true temperature obtained by ellipsometry, T_{ellips}, and that obtained by other methods, T_{indic}, including a thermocouple embedded within the substrate holder (lines and open points) and a pyrometer (filled points).

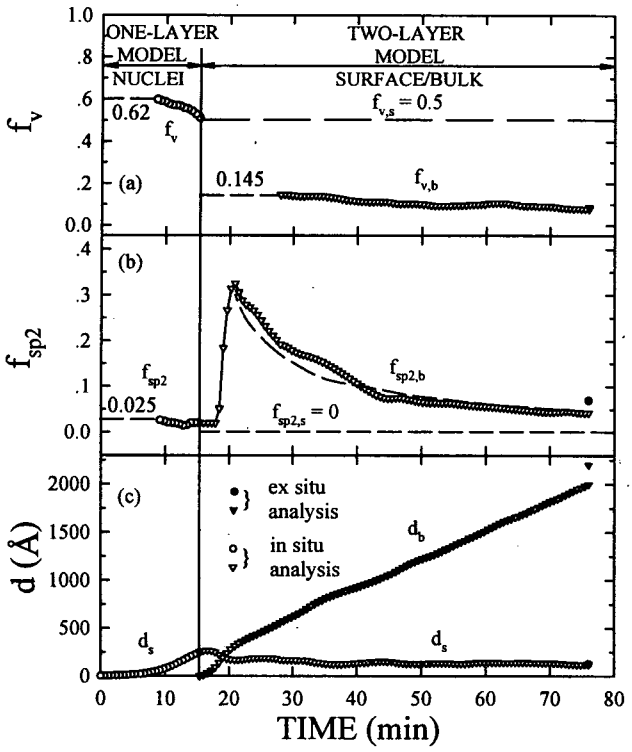

Fig 3. Evolution of the microstructure during MPECVD diamond film growth, deduced from an analysis of real time spectroscopic ellipsometry data. The surface temperature, plasma power, pressure, and $CH_4/(CH_4+H_2)$ gas flow ratio were 785 ℃, 500 W, 7 Torr, and 1 %, respectively. $d_{(b,\ s)}$ are the bulk (b) and surface (s) roughness layer thicknesses. $f_{v,b}$ and $f_{v,s}$ are the void volume fractions in the bulk and surface layer; $f_{sp2,b}$ and $f_{sp2,s}$ are the sp^2 C volume fractions in the bulk and surface layer, respectively.