

Chemical Vapor Deposition of Fluorocarbon Films for Low Dielectric Constant Interlayer Dielectric Applications

by

Brett Alexander Cruden

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Abstract

The objectives of this work are: 1) to evaluate the suitability of fluorocarbon films deposited by chemical vapor deposition (CVD) for use as an interlayer dielectric on microelectronic chips; and 2) to characterize the deposition process. Two varieties of CVD have been used: Pulsed Plasma CVD (PPCVD) and Pyrolytic CVD. The pyrolytic CVD process uses a heated surface to decompose the precursor gas, forming reactive CF_2 species, which then deposit on a cold substrate to form CF_2 chains. In the pulsed plasma CVD process, the precursors are dissociated by a plasma to produce fluorocarbon films. These films tend to be more cross-linked, and less like polytetrafluoroethylene (PTFE) than the pyrolytic films. Pulsing the plasma is found to be effective in controlling the film composition and degree of cross-linking.

To integrate a low dielectric constant (low k) material into current device processing schemes, the film must be able to withstand temperatures up to 400 °C without degradation. We have created a simple, yet novel apparatus for examining thermal stability. This apparatus uses interferometry to track film thickness loss as a function of temperature. At least two modes of decomposition have been observed. The mechanics of decomposition differ based on the degree of cross-linking. Oxygen incorporated into plasma films on atmospheric exposure is seen to degrade the thermal stability. Free radical sites, left behind by the plasma deposition process, will incorporate unstable oxygen groups and can also contribute directly to decomposition. Examination of decomposition in different environments (oxygen, nitrogen, hydrogen and fluorine) has allowed us to further identify pathways for the decomposition process. More cross-linked films will cleave at sterically strained bonds, forming multiple radical centers which then react readily with the environment. Films with less cross-linking will tend to eliminate short fluorocarbon chains and are less susceptible to oxygen attack. Some films have shown an improvement in thermal stability by *in-situ* annealing following deposition. However this improvement comes by decomposing weaker film moieties, and is thus associated with significant film loss. The majority of plasma films we have produced fall into a thermal stability minimum with respect to cross-linking. While greater cross-linking will improve thermal stability, it also can raise dielectric constant significantly. A lower degree of cross-linking should improve thermal stability (based on what is known about fluoropolymers) while maintaining a low dielectric constant.

However our work demonstrates this low degree of cross-linking is not achievable by plasma CVD.

The second major aspect of the work involves the characterization of the CVD process. UV Adsorption spectroscopy is used in this work to study gas phase transients of CF_2 , the desired deposition precursor. Time resolved UV adsorption measurements are used in combination with an elementary mole balance model to model the chemistry of the unsteady state pulsed plasma. CF_2 production is observed during the plasma off time and is affected by chamber wall temperature, consistent with other literature observations of CF_2 surface production. The temperature dependence suggests that CF_2 is produced from film rearrangement. Film composition is observed to correlate well with gas phase CF_2 concentration. The pyrolytic CVD process is also characterized in how CF_2 concentration related to deposition rates. It is seen that the apparent sticking coefficient of CF_2 is quite low, suggesting very slow growth rates from CF_2 alone. It is likely that oligomers of CF_2 , formed in the gas phase, are important to deposition.

Thesis Advisors:

Herbert H. Sawin

Professor of Chemical Engineering and Electrical Engineering and Computer Science

Karen K. Gleason

Associate Professor of Chemical Engineering