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Solid-Vapor multiphase plasma: Mesoplasma processing
固一気マルチフェーズプラズマ メゾプラズマ反応場の応用

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Mesoplasma can be distinguishably defined as a plasma in the 0.1 – 10 Torr range which possesses the characteristics of both low pressure and thermal plasmas. Upon application of such a non-equilibrium plasma flow to chemical vapor deposition, formation of controlled growth precursor similar to the low pressure plasma and its fast transport toward the substrate at high flux are anticipated, which coincides with the requirements of the technologies for large scale production of functional devices/materials. In the case of Si deposition by CVD as one example, it is revealed that liquid like nanoclusters are formed as precursor and their unique dynamics facilitate fast rate Si epitaxial film deposition. In such a way, mesoplasma potentially offers a unique environment for simultaneous attainment of quality and production speed.

1. Introduction

Recent devices in many applied fields require mostly simultaneous attainment of functionalities and low cost, and thus seek for production routes that combine high quality and high throughputs. In respond to such a demand, especially related to film deposition, a plasma in the 0.1 – 10 Torr range is expected to offer a non-equilibrium plasma flow environment in which selected species are formed and transported toward substrate at high flux. One of the important characteristics is that, in contrast to the 3D space associated with formation deposition precursor for the conventional low pressure processing, a space for precursor formation can be confined in the 2D region in this pressure range because of gas flow characteristics of mesoplasma. As a result, despite the difference in the mean free path of such species between these pressures, Knudsen number under mesoplasma can be comparably as large as that under low pressure environment. If active species for deposition form through cooling of high temperature chemistries within the 2D space that is present at the tail of mesoplasma flow ahead of the substrate, the deposition itself can be controlled as nicely as low pressure processing, while maintaining rather fast rates owing to its flow dynamics under high density environment. In fact, we have demonstrated fast rate deposition of silicon epitaxial films that maintain wafer-equivalent qualities under the mesoplasma condition [1]. This in turn suggests that the deposition precursors that potentially formed within the 2D region could have a clue to this unique characteristic of the mesoplasma processing.

2. Formation of liquid–like nanoclusters as deposition precursors

In the case of the thermal plasma chemical vapor deposition, raw materials that are introduced into the plasma in a form of either gas, liquid or powder are decomposed completely to atomic state at high temperature, and these vapors are expected to condense within the 2D thermal boundary region present ahead of substrate. However, unlike the nanoparticle formation for thermal plasma CVD, less agglomerated species with several nanometer in size are expected under the mesoplasma condition because of the condensation in a reduced pressure. To identify such species that are potentially in several nanometer immediately after nucleation, x-ray scattering was employed to detect them in-situ within the 2D reaction space during CVD. In brief, x-ray was introduced into the thermal boundary region with several 100 μm parallel to the substrate surface such that potential growth precursors scatter x-ray spatially and analysis of the scattering intensities provides the size and structure of the scatterers. Details of the measurement system can be found elsewhere [2,3].

Although no significant scattering signal of the incident x-ray (Cu-Kα) was monitored under vacuum or Ar plasma condition, appreciable scattering intensity was detected from the region of the 2D at a wide angle only when the source gas was introduced. If atomic Si is present in the 2D region, scattering decreases and transmission increase because of its smaller cross section than Ar. Therefore, this is an evidence that objects are not atomic species that scatter the x-ray. Furthermore, small angle X-ray scattering revealed that the objects are several nm in size and have a rather loosely bound structure. Interestingly, the scattering signals for the condition that the polycrystalline films are deposited has suggested the formation of relatively large scatterers with liquid-like structure similarly observed for the precursor for epitaxial growth. It is therefore evidently identified that nanosized clusters with liquid like atomic structure plays determinant role in the film structural control during fast rate CVD.

3. Unique dynamics of nanoclusters during impingement on substrate

Molecular dynamics (MD) simulation was employed to reproduce formation of nanoclusters through rapid condensation of high temperature Si vapors and so to elucidate their roles in fast rate epitaxy. Detailed computational conditions can be found elsewhere [4]. It is confirmed that a several nm sized cluster having a loosely bound structure forms as a transitional quasi-stable condensed phase at a certain degree of undercooling during continuous cooling before the constituent atoms are ordered to form a crystal at low temperature. Such a liquid like structure was observed for relatively large clusters and also for the binary system of Si-H. Furthermore, during impingement of these clusters on a substrate, globular clusters are found to exhibit instantaneous deformation, allowing the constituent atoms at least near the cluster / substrate interface to rearrange their positions to follow the underlying crystal structure. As a result, epitaxial film deposition itself was reproduced after multiple impingement of these liquid like clusters. For a large cluster having 5 to 8 nm in size, in contrast, although the structure was confirmed to be similarly loosely bound, the constituent atoms far away from the interface was not properly ordered, resulting in the amorphous / polycrystalline structural formation. This proves therefore that the cluster determines the film structure and thus the quality. Also, since high degree of sticking of clusters is observed in the present simulation, cluster could also be a key to attain fast rate deposition. Several MD simulations have reported that epitaxial growth was attained by deposition of nanosized clusters on the condition that they are given enough high kinetic energies to promote surface diffusion. In contrast, the cluster created during rapid condensation does not necessarily require such a large kinetic energies for epitaxy. This is additional uniqueness of the clusters formed in the mesoplasma processing.

4. Summary and prospects

Liquid like cluster formed in the mesoplasma environment can be an unique deposition precursors that offer potentially both fast rate and reasonable high quality. Under such a non-equilibrium condensation, we can also use the chemical non-equilibrium, in a way that high temperature stable chemistries are frozen-in. In the case of Si production from $SiHCl_3$ (TCS), $SiCl_4$ (STC) that is stable at low temperature limits the conversion of TCS to be only around 30% at the maximum if the process based on the equilibrium chemistries is employed. Under mesoplasma, in contrast, high temperature gas vapors at temperature where STC is no longer stable can be directly utilized for deposition precursor formation, resulting in an improved conversion yield of ~60 % [6].

Similar to Si nanoclusters for Si epitaxy, one can expect multi-component clusters for alloy phase single crystal. For example, SiC is expected in a variety of devices ranging from high temperature semiconductor to next generation jet turbine, both of which by nature require high quality and large quantities. Unlike Si, SiC sublimates and no congruent melt exist under equilibrium, which is why this material is synthesized primarily by Si_2C and SiC_2 stable molecules. It is therefore expected that liquid-like SiC cluster forms as a transitional precursor and facilitates fast rate SiC epitaxy imilar to Si epitaxy. In such a way, mesoplasma processing may open up a novel production path of quality products of multicomponent.

Acknowledgments

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