論文の内容の要旨

論文題目： Cluster-enhanced high-rate and low-temperature silicon epitaxy
by mesoplasma chemical vapor deposition
(クラスター支援メゾプラズマＣＶＤによるＳｉ厚膜の高速低温エピタキシー成長)

氏　名： ディアズ　ホセマリオ　アバンテ
(Jose Mario Abante Diaz)

The deposition of highly oriented crystalline silicon films at high rates and low temperatures has been of technical and scientific interest, especially in the fabrication of large-area electronic devices where micron-thick epitaxial films are required in order to reduce their cost. Particularly in the photovoltaic industry, the prices of the raw materials such as silicon, ingots/wafers, cells and modules make up more than 55% of the total production costs, and these have continuously risen in the past years. In addition, there is presently a shortage in solar grade silicon raw material which further contributes to the increase in the total price of a finished solar module. This study is thus motivated by the need to develop a new processing route for device-grade epitaxial silicon films.

Several high-rate epitaxial deposition techniques have attained rates of around 10 – 100 nm/s at temperatures higher than 650 °C. However, high deposition temperatures result in autodoping from and dopant redistribution in the underlying film or substrate, which are otherwise negligible in low-temperature processing. However, epitaxial deposition at low temperatures is in general limited by low deposition rates and the presence of a critical epitaxial thickness, beyond which, the transition from epitaxial to amorphous or polycrystalline film growth occurs. The latter is considered to be mainly due to defect accumulation, kinetic surface roughening or impurity segregation. As a result, the majority of studies on epitaxial deposition at temperatures less than 650 °C have reported deposition rates ranging only from 0.02–1.2 nm/s and thicknesses less than a few microns. From a scientific perspective, the development of a new process would require looking beyond the aspects, mechanisms and approaches of conventional processes and techniques. This presents a very interesting and challenging theme both from an experimental and theoretical point of view.

In view of the limitations of the existing silicon deposition techniques, the so-called "mesoplasma" chemical vapor deposition (CVD) technique will be established as a new epitaxial silicon thick film processing route that potentially satisfies both the device performance and economic demands of the industry. This study aims to gain a fundamental understanding of the deposition and growth mechanisms in mesoplasma epitaxy. Particular focus is given to these three aspects which will provide the basic information to obtain a general picture of the mesoplasma process and highlight its unique characteristics from other existing techniques: (a) the simultaneous attainment of high rate and low temperature epitaxy will be demonstrated by investigating key process parameters, namely, source gas (silane) partial pressure and substrate temperature; (b) understanding of precursor/nanocluster formation within the mesoplasma and its role in epitaxy will be elucidated through an in-situ X-ray scattering technique within the gas phase, applied for the first time in such a dynamic environment; and (c) the influence of hydrogen, a key element which has been known to affect silicon epitaxy, in nanocluster-surface and plasma-surface interactions will be investigated.

Mesoplasma CVD

From a processing point of view, the mesoplasma is described as a plasma generated in the 0.1 to 10 Torr range with a high gas flow rate. It is also characterized by its relatively low electron, T_e and gas temperatures, T_g, and values of $T_e < 1\,\mathrm{eV}$ and $1 < T_e/T_g < 10$ are anticipated. Under these conditions, effective source gas dissociation and low ion bombardment on the substrate is attained while maintaining relatively moderate to low deposition temperatures compared to thermal plasma processing, thus, making high-rate deposition of thick films at relatively low temperatures possible. In addition, due to the relatively low electron temperature, the dominant plasma chemistry is controlled by atoms and significant ion bombardment on the film leading to degradation of properties is minimized.

In mesoplasma CVD, a thermal boundary layer exists between the plasma and the substrate where vapor condensation and nucleation take place. These processes are expected to contribute to the generation of atomic and nanometer-sized silicon clusters which will subsequently act as the deposition precursors to film growth. The nature of the atoms and clusters, such as cluster size, size distribution and cluster energy, may be controlled through the boundary layer to form a variety of film structures, including epitaxial films, while maintaining the high flux of the precursor and a low substrate temperature.

High-rate and low-temperature silicon epitaxy

Mesoplasma epitaxy is carried out using a radio frequency (rf) inductively-coupled plasma CVD system at a fixed total pressure of 6 Torr and rf power of 22 kW. Argon is used as the main plasma gas while silane, (SiH_4) diluted with 20% hydrogen serves as the source gas. In order to simultaneously attain high-rate and low-temperature epitaxy, the amount of silane and substrate temperature were systematically varied. Increasing the amount of silane resulted to a linear increase in deposition rate which is independent of the substrate temperature, indicative of adhesive growth. Interestingly, despite increasing deposition rates and decreasing substrate temperatures, the structural and electrical properties of the epitaxial films are maintained. A high epitaxial deposition rate of around 35 nm/s was achieved even at substrate temperatures as low as 360 °C, while maintaining the Hall mobility values to around 270 cm^2/V-s. Such a combination of deposition rate, temperature and film quality has never been reported for other deposition techniques. With mesoplasma CVD, epitaxial films with thicknesses of several tens of microns can easily be deposited within a few minutes. From a processing perspective, this would translate to significant reductions in cost.

The temperature independence of the deposition rate and electrical properties is also unlike the behavior observed for conventional deposition techniques. Because the power was held constant in the previous set of experiments, the boundary layer thickness did not vary much and precursors having generally similar characteristics were generated. This could suggest the uniqueness of the deposition precursors associated with epitaxy in mesoplasma CVD.

Nanocluster role in epitaxy

As stated previously, the condensation of atomic silicon within the thermal boundary layer results to the generation of nanoclusters. Detection and characterization of the silicon nanoclusters, as they are formed in the vapor phase, is an essential key to gain fundamental understanding about the deposition mechanism and to establish better control in the mesoplasma CVD process. Utilizing a laboratory-scale X-ray generator and a two-dimensional position-sensitive proportional counter, a small-angle X-ray scattering system was constructed and incorporated to the existing mesoplasma CVD chamber. Through the SAXS system, free silicon nanoclusters generated in the gas phase have been successfully detected in situ during silicon film deposition. Spherical nanoclusters acting as deposition precursors around 2 nm in size were identified and associated with epitaxial film growth. These nanoclusters were characterized to have a diffuse electron density distribution in the vicinity of the nanocluster surface, which is indicative of a loosely-bound structure, the so-called "hot cluster". Due to the thermal energy provided by the plasma, the atoms comprising the nanoclusters responsible for epitaxy are loosely-bound and in a non-rigid and thermally energized state. The high internal energy thus facilitates cluster deformation upon impingement even on a relatively low temperature substrate, allowing the individual atoms to migrate on the surface for lateral growth, leading to high quality films. On the other hand, the emergence of a small amount of larger clusters with a relatively rigid form was associated with the transition from an epitaxial to agglomerated film structure.

By simple control of the deposition parameters, the nanocluster characteristics can be effectively controlled in mesoplasma CVD. This nanocluster-based approach for film deposition by mesoplasma CVD has great potential for depositing device quality films simultaneously at high rates and low temperatures, which are otherwise not attainable with other deposition techniques. The potential of SAXS as an in situ plasma diagnostic technique has also been demonstrated. Further improvements could eventually establish SAXS as an effective plasma diagnostic tool for real-time and in situ process monitoring and control.

Plasma-nanocluster-surface interactions – influence of hydrogen

Hydrogen, which is present as the diluent gas and generated from the inevitable decomposition of silane, is known to affect silicon epitaxy, especially at low temperatures. Thus, in mesoplasma epitaxy where the gases are highly dissociated, atomic hydrogen is expected to influence the deposition process. Numerous investigations describing the effects of hydrogen have been reported, some even with totally contradicting claims. At low temperatures, some assert that atomic hydrogen enhances epitaxy by promoting the surface diffusion of precursors, or by abstracting adsorbed surface hydrogen to expose available sites for silicon bonding. Still, other models report that hydrogen has a disruptive role in epitaxy by segregating on the surface leading to defect formation, or by causing a buildup of surface roughness due to limited adatom mobility. Regardless of whether hydrogen is favorable or detrimental to epitaxy, it is generally known that the effect is chemical in nature. In the investigation of the effect of hydrogen in mesoplasma CVD, the approach involves looking into two critical aspects of the deposition process, namely, on the generation of in-flight deposition precursors and on the evolution of film morphology and structure. Identifying which aspect is critically affected by hydrogen could enable more effective control of the deposition process and further improvement of the electrical properties.

Through SAXS, the effect of varying amounts of hydrogen on the characteristics of the nanoclusters was studied. It was found that at fixed values of rf power, substrate temperature and silane corresponding to epitaxy, varying the hydrogen partial pressure from 150 to 460 mTorr does not critically alter the characteristics of the nanoclusters (~ 2 nm in size) as growth precursors. The nanoclusters exhibit similar characteristics as the nanoclusters previously associated with epitaxy, that is, having a loosely-bound, non-rigid structure. However, examination of the deposited films revealed that at hydrogen partial pressures less than 220 mTorr, the film exhibited a polycrystalline structure, whereas at higher hydrogen partial pressures, the films are epitaxial with Hall mobilities exceeding 200 cm^2/V-s. Another set of experiments involving exposure only to an Ar-H_2 plasma under varying hydrogen partial pressures showed that the silicon substrate surface is smoother with increasing hydrogen introduction. At high hydrogen amounts, the chemical effect of hydrogen is likely promoted and provides favorable conditions for the atoms of the nanoclusters to migrate on the substrate surface and incorporate at step edges or kinks. Thus, in order to effectively utilize the unique nanocluster characteristics to attain epitaxy, a minimum amount of hydrogen is needed. It is concluded that the interplay of the nanoclusters characteristics and the hydrogen-surface interaction is a key to further improve the deposition process.

The aforementioned results have demonstrated the unique features and advantages offered by mesoplasma CVD. The advancements gained in the study, both from scientific and technological perspectives could pave the way for the eventual establishment of the mesoplasma CVD as a new processing route for the fabrication of high quality epitaxial silicon films at high rates and low temperatures.