Plasma production of polymorphous silicon thin films:
application to large area electronic devices

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Large area electronics is an expanding field, which, as microelectronics, is based on plasma processes. In particular, silane plasmas have been largely studied and the produced amorphous silicon thin films (a-Si:H) are the basis of a large number of devices (solar cells, thin film transistors, photo and particle detectors,...) [1]. When transferring the research results into production, deposition rate is one of the key issues. However the increase in deposition rate from typically 0.1 nm/s up to a few tens nm/s generally results into the formation of powder. Thus, the subject of dusty or complex plasmas [2] has experienced a large development in the last decade and brings us to the topic of this paper: not the dust itself but the dust precursors. Indeed, to begin with, we were interested to understand powder formation in order to avoid it or to manage it, as powder is associated with the achievement of high deposition rates. However, from the study of square-wave modulated discharges we could observe the formation of silicon nanocrystals (powders precursors) even at room temperature [3,4]. This finding completely changed our strategy and pushed us to work under plasma conditions at the onset of powder formation [5]. The aim was and remains to produce nanostructured silicon thin films under plasma conditions where silicon clusters, nanoparticles and crystallites are formed. Among these nanostructured materials we have recently focused on polymorphous silicon (pm-Si:H) which shares the high optical absorption of a-Si:H while having improved transport properties. A material which has different crystalline forms is defined as polymorphous, and indeed, besides the diamond structure we have observed silicon crystallites with a hexagonal structure [6].

In this presentation we summarize our recent work on the synthesis and the characterization of pm-Si:H, as well as the study of devices based on this new material.

Plasma and in situ growth studies show that pm-Si:H films are clearly distinct from amorphous, protocrystalline and microcrystalline materials [7]. While the detection of nanometer size silicon particles in the plasma remains a challenging issue, some techniques such as cavity ring down, photon counting experiments and impedance measurements emerge as the techniques able to guide the optimization of the size and density of nanoparticles contributing to deposition. Moreover growth studies in which the thermophoretic force between the electrodes is adjusted in order to move the nanoparticles towards or away from the substrate, have unambiguously demonstrated the importance of the nanocrystallites and/or clusters in pm-Si:H deposition [7]. Besides clusters, the conditions of pm-Si:H deposition involve a large amount of ions with respect to a-Si:H deposition [8]. These differences in the growth precursors are reflected in the growth kinetics as well as in the film structure.

X-Ray, Raman and high resolution transmission microscopy measurements show that besides the presence of a small amount of crystallites (less than 10%), the amorphous matrix is more relaxed than that of a-Si:H and it presents some medium range order, which can be held responsible for the improved electron and hole transport properties, both in the as-deposited and light-soaked states [9]. Indeed, as a-Si:H, pm-Si:H films show large changes in the electronic properties when exposed to light soaking. The metastability of both materials is
related to their hydrogen bonding, much more rich in the case of pm-Si:H films, and which can be related to the hydrogen bonded at the surface of the clusters and crystallites, resulting in new absorption bands in the infrared absorption as well as on new hydrogen evolution peaks.

The outcome of these materials studies reflects on the operation of electronic devices. Indeed, while powders can introduce electronic defects, the same does not apply for nanoparticles which can relax the amorphous matrix and lead to better electronic properties. As a matter of fact, we are able to produce better devices by using pm-Si:H in pin solar cells [10].

As a conclusion, low pressure silane plasmas are an interesting way of producing nanocrystalline silicon particles. When incorporated in an amorphous matrix, we obtain nanostructured materials such as polymorphous silicon which are a challenging alternative to a-Si:H in the field of large area electronics. Moreover, the precise control of the size and concentration of nanocrystalline silicon particles in the plasma should open the way to the nanoelectronics field in which the plasma produced nanocrystallites can be passivated, coated,... and finally incorporated in devices such as non volatile memories. This is in our opinion an important challenge for the plasma community for the next few years.

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