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Role of the substrate on the growth of silicon quantum dots embedded in silicon nitride thin films

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HIGHLIGHTS

- The influence of the substrate surface profile for the growth of SiQDs is studied.
- The influence of the substrate chemistry for the growth of SiQDs is studied.
- Substrate surface profile influence on the growth of SiQDs by RPECVD is minimal.
- Frank–van der Merwe mechanism will promote the growth of embedded SiQDs.
- Volmer-Weber mechanism will not promote the growth of embedded SiQDs.

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ABSTRACT

By using a remote plasma enhanced chemical vapor deposition system, we grow a silicon rich silicon nitride thin film on the surface of five different substrates: silicon wafer, fused silica, highly oriented pyrolytic graphite, muscovite mica and potassium chloride. By means of high-resolution transmission electron microscopy we studied the influence that each substrate has on the auto-formation of silicon quantum dots ($\leq$4.2 nm) embedded in the grown film. We conjecture that the growth of the film is carried out by the formation of highly reactive intermediates that are chemisorbed on the substrate surface. We conclude proposing the hypothesis that the substrate surface profile has minimal influence on the growth of a silicon nitride thin film that can embed silicon quantum dots.

1. Introduction

A proper control of the luminescence from silicon quantum dots (SiQDs) would allow their commercial use in technologies ranging from artificial lighting to optical computing applications [1–5]. In Remote Plasma Enhanced Chemical Vapor Deposition (RPECVD) technique, it is possible to imbibe a field of SiQDs in a silicon nitride thin film by changing the proportion of gases that give rise to a silicon nitride stoichiometric film [6,7]. Therefore, it is appropriate to call silicon-rich silicon nitride (SR-Si_3N_4) thin films to the embedded systems, because the silicon excess in the growth process is the responsible of the SiQDs auto-formation [6,8,9]. In this sense, the SR-Si_3N_4 films could be an excellent option for technology transfer because Si_3N_4 has a good concentration of charge carriers and a moderate band gap that enables low turn on voltages in operational devices [7,10].

Multiple studies have shown that quantum confinement effect is to a great extent responsible of the absorption-emission characteristics of SR-Si_3N_4 systems [5,11–14]. In other words, in a SR-Si_3N_4 system it is possible to tailor (within certain limits) absorption, emission or both by changing the SiQDs average size and population density. This design capability make these systems very attractive because they can be used not only in electroluminescent or optoelectronic devices but also in sensors and solar cells [15–18].

On this subject, one of the main motivations for studying the substrate influence on the growth of SiQDs is to identify the invariability of the grown film, which is a requirement for the complete characterization of a particular thin film under study. For instance, to evaluate the photoluminescence emission spectrum,

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monocrystalline silicon wafers are used; meanwhile to perform absorbance measurements a fuse silica substrate is required. But additionally, it is pertinent to remember that both microelectronic devices and solar cells are constructed by the successive deposition of thin films with different functions and therefore compositions. In consequence, it is of great importance to know the final characteristics of the SR-Si_3N_4 systems growth on different substrates, especially those that are most used in microelectronics and photovoltaic industries.

In this regard some research groups have carried out studies about the SiQDs growth on the surface of the following substrates: n-type single crystalline silicon, corning glass, fused silica, and amorphous silicon nitride [19], SiO_2 with different surface densities of Si-OH [20], and highly oriented calcium fluoride [21]. In the previously mentioned works the authors use Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) as their main analysis tools, they conclude in a non-definitive way that two phenomena are responsible of the SiQDs formation and their final characteristics. The phenomena are, in first place the chemical interaction between the precursor gases and the substrate surface, and secondly the surface profile of the substrates. Unfortunately, due to the SiQDs self-forming nature, it is not possible to confirm by AFM and SEM whether the agglomerations are quantum dots, an initial nucleation of the silicon nitride matrix or a combination of both.

In this paper we have done a comprehensive study based primarily on High Resolution Transmission Electron Microscopy (HRTEM) in order to report the SiQDs characteristics of five SR-Si_3N_4 systems, each one growth on the surface of the following substrates: n-type single crystalline (100) silicon wafer, fused silica, highly oriented pyrolytic graphite (HOPG), muscovite mica and single crystalline potassium chloride. We found that the growths on single crystalline silicon and fused silica have SiQDs with better characteristics i.e. reduced average size and high population density, these two substrates are followed by the HOPG which also exhibits acceptable SiQDs properties. Meanwhile muscovite mica and potassium chloride show the worst SiQDs characteristics i.e. bigger average sizes and populations without normal distributions. We conclude that chemical affinity between the substrate and the precursor gases used to grow the silicon nitride film is the most important parameter in order to achieve SiQDs formation and reproducibility.

2. Experimental details

Silicon-rich silicon nitride thin films investigated in this work were grown using a RPECVD system assembled by MVS Inc. Company. A full description of the RPECVD characteristics, including a detailed layout of all components can be found in a previous work [22]. In order to perform the analysis of the relationship between the substrate chemistry and the growth of a SR-Si_3N_4 thin film, it is appropriate to recall that our RPECVD system has a vacuum reaction chamber. Within the chamber, the gas dissociation process is carried out and it is followed by the conformation of the silicon nitride thin film. Fig. 1 shows a simple scheme of this chamber, it is convenient to identify that the chamber is a continuous space. However the horizontal dotted line divides it into two virtual sections. This virtual division is useful for describing and analyzing the processes involved in the growth of the silicon nitride thin film.

In the first virtual section is located a coil coupled to a radiofrequency (RF) source. The RF produces energetic electrons which allow the molecule dissociation of the supplied gases (Ar, NH_3, SiH_2Cl_2, H_2). The first section is far enough (≈ 100 mm) from the location of the substrates (2nd virtual section), for that reason the radiofrequency and its energetic electrons (in Fig. 1 delimited by the dotted oval) will have no influence on the substrates surface nor in the film that grows there.

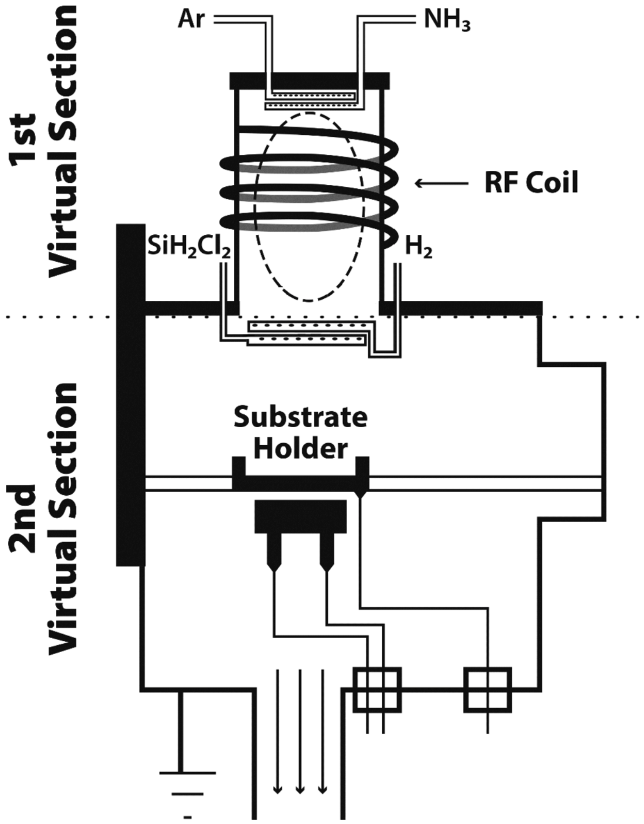

Fig. 1. Scheme of the RPECVD reaction chamber used to growth the SR-Si_3N_4 thin films of this study. This reaction chamber is a continuous space. Two sections were marked in the scheme to indicate that different processes occur in each section.

All films were grown using the following parameters: 1) Gas mixture of SiH_2Cl_2, H_2, NH_3 and Ar with flow rates of 5, 20, 200 and 75 sccm. 2) Chamber pressure of 0.30 Torr. 3) Substrate temperature of 300 °C and 4) Radio frequency power (13.56 MHz) of 150 W.

The SR-Si_3N_4 films were deposited on five different substrates: P-type single crystal (100) low resistivity (5-20 Ω-cm) silicon wafer, Fused silica, Highly Oriented Pyrolytic Graphite SPI grade 3 (HOPG), Muscovite mica and Potassium chloride. The silicon wafers were supplied by Wafer World, Inc., fused silica was bought from Sigma-Aldrich, HOPG substrates were purchased from Structure Probe, Inc., muscovite mica was obtained from Ted Pella, Inc., and the potassium chloride was grown on our crystal grow laboratory. Table 1 indicates the chemical compositions (reported by the supplier) of each substrate used for this study.

Prior to deposition and in order to remove native oxide, silicon substrates were dipped during 180 s in “p-etch solution” (300:15:10 parts of H_2O: HNO_3:HF), subsequently the substrates were rinsed with deionized water and the drying process was carried out using nitrogen gas. Fused silica substrates were solvent cleaned with trichloroethylene, methanol and acetone with a previously reported method [23]. The substrates HOPG, muscovite mica and potassium chloride were cleaved prior to the deposition of the SR-Si_3N_4 thin films.

The surface profile of the substrates was measured by atomic force microscopy (AFM) using a Jeol JSPM-4210 on tapping mode and a high resolution Mikromasch NSC15 silicon tip with radius of curvature <10 nm. The AFM images were processed using WSxM 5.0 software [24]. The observation of SiQDs was carried out by