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Commentary

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Low-Temperature Fabrication of Silicon Nitride Thin Films from a SiH4+N2 Gas Mixture by Controlling SiNx Nanoparticle Growth in Multi-Hollow Remote Plasma Chemical Vapor

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DESCRIPTION

Silicon nitride (SiNx) is widely used in Si and III-V electronic and optoelectronic technologies [1]. For example, SiNx thin films are used as the passivation layer to protect semiconductor devices and as the gate dielectric layer in Thin-Film Transistors (TFTs) [2]. Research on SiNx thin films has been directed towards improving the control of the hydrogen content, refractive index, and extinction coefficient of light.

For the formation of SiNx films at low temperature, Plasma-Enhanced Chemical Vapour Deposition (PECVD) has been mainly used [3]. PECVD allows SiNx deposition at ~300 °C, in contrast with low-pressure Chemical Vapour Deposition (CVD) (>700 °C). However, it has disadvantages, such as plasma-induced damage and a thermal budget [4], which may lead to decreased device performance of TFTs. Furthermore, to meet the demand for next generation electronic products, wearable devices and flexible displays are expected to utilize flexible substrates, such as polyimide or polyethylene terephthalate (PET) [5].

Furthermore, SiNx films fabricated by PECVD at low substrate temperatures (<100℃) are typically not stoichiometric (with N/Si < 1) and H contain over 1×1022 cm-3, resulting in localized states and instability in device performance [6]. Therefore, the objective of this study is to develop a SiNx film with high nitrogen content (N/Si>1) and low hydrogen content (<1×1022 cm-3) that can be fabricated at low substrate temperatures (<120℃).

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Therefore, the fabrication of amorphous SiNx thin films via controlled growth of nanoparticles in SiH4 + N2 mixture using remote plasma CVD [7, 8] at low substrate temperature 100 °C was reported. These findings indicates that small Si nanoparticles could be nitrided in the plasma phase, and subsequently incorporated into the films, resulting in a high N/Si ratio (~1.24) and low hydrogen content (~8.7 × 1020 cm−3).

A unique feature of this research was the capability to accurately control the size of SiNx nanoparticles by using remote multi-hollow electrode [7, 8]. The primary factors responsible for nanoparticle growth were the density of precursor radicals and gas residence time. Therefore, the nanoparticle size was controlled by tuning the N2/SiH4 flow rate ratio and the total gas flow rate in this study. Three Quartz-Crystal Microbalances (QCMs) and Transmission Electron Microscopy-Energy-Dispersive X-ray Spectroscopy (TEM-EDS) measurements revealed that a higher degree of nanoparticle incorporation in the SiNx film corresponded to a larger N/Si ratio and lower hydrogen content in the film, which implied that the nanoparticles were nitrided in the plasma phase. These results were attributed to the small heat capacity and large specific surface area of the nanoparticles, which facilitated the active chemical reaction on their surface in the plasma.

These results demonstrate that Si–N bonds were formed and Si–H and N–H bonds were broken in the nanoparticles at high temperatures [9] during the plasma phase despite the low substrate temperature. This is similar to the annealing process, which induces the release of hydrogen. Under appropriate annealing temperature and time, defects are passivated in the bulk, followed by the breaking of Si–H bonds (~3.1 eV) and then N–H bonds (~4.1 eV) [10]. The SiNx thin films were fabricated by high-quality SiNx nanoparticles with diameter of a few nm and SiH - based radicals. Thus, a SiNx thin film with a higher N/Si ratio and smaller hydrogen content can be fabricated at a low substrate temperature of 100 °C under experimental conditions where small nanoparticles are generated in the plasma. This study provides new insight into the role of small nanoparticles in the fabrication of SiNx thin films, not only for remote plasma CVD but also for the other commonly used techniques, ICP and capacitively coupled plasma-enhanced CVD.

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