Highly Porous Silicon Membranes Fabricated from Silicon Nitride/Silicon Stacks
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Nanopore formation in silicon films has previously been demonstrated using rapid thermal crystallization of ultrathin (15 nm) amorphous Si films sandwiched between nm-thick SiO₂ layers. In this work, the silicon dioxide barrier layers were replaced with silicon nitride, resulting in nanoporous silicon films with unprecedented pore density and novel morphology. Four different thin film stack systems including silicon nitride/silicon/silicon nitride (NSN), silicon dioxide/silicon/silicon nitride (OSN), silicon nitride/silicon/silicon dioxide (NSO), and silicon dioxide/silicon/silicon dioxide (OSO) were tested under different annealing temperatures. Generally the pore size, pore density and porosity positively correlate with the annealing temperature for all four systems. The NSN system yields substantially higher porosity and pore density than the OSO system, with the OSN and NSO stack characteristics falling between these extremes. The higher porosity of the Si membrane in the NSN stack is primarily due to the pore formation enhancement in the Si film. We hypothesize that this could result from the interfacial energy difference between the silicon/silicon nitride and silicon/silicon dioxide, which influences the Si crystallization process.

1. Introduction

Ultrathin porous nanocrystalline silicon (pnc-Si) membranes fabricated by crystallizing amorphous silicon thin films deposited by rf sputtering were first published by Striemer et al. in 2007.[1] The advantages this new nanoporous membrane offers over other nanoporous membranes were clear. First, the ultrathin nature of this membrane, only a few tens of nanometers thick, is comparable to the size of many biomolecules. As a result, mass transport through this membrane is greatly enhanced as compared to traditional tortuous path polymer membranes.[2] Another advantage is the simple and inexpensive fabrication process, involving a bottom-up approach, rather than a top-down lithographic approach that other porous nano-membranes rely on.[3] Nanopores are spontaneously formed in silicon during rapid thermal annealing of ultrathin (~15 nm) amorphous Si films sandwiched between nm-thick SiO₂ layers deposited on a Si wafer, a novel phenomenon that had never reported before. A lot of research has been conducted to utilise this unique porous membrane.[4–9] Applications range from biological and gas separations to use as sensors (pressure, temperature, biological) or as a platform for electron imaging and spectroscopy.[4–9]
Our previous results have shown that one of the prerequisites for the nanopore formation in the silicon film is the presence of both top and bottom SiO$_2$ layers. The top SiO$_2$ layer prevents the silicon film from agglomerating while the bottom SiO$_2$ layer works as a barrier layer to prevent homoepitaxy from the Si wafer during annealing. Recent results by Balachandra Achar et al. confirm our results even though their deposition technique was different and they used much thicker SiO$_2$ layers. Experimenting with barrier layers other than silicon dioxide could be a first step toward generalizing the phenomenon to other material pairs. Silicon nitride, another dielectric material with favorable optical properties, high thermal stability, chemical inertness, and good dielectric properties, has been widely used in optoelectronic devices and integrated circuit fabrication processes such as gate dielectrics, diffusion barriers, isolation materials and final passivation layers.

In this work, we incorporate silicon nitride as an alternative barrier layer in stack geometries including nitride/silicon/nitride, oxide/silicon/nitride and nitride/silicon/oxide (NSN, OSN and NSO), and demonstrate for the first time that silicon nanopores can also be spontaneously formed by these thin film stacks. The porosity, pore density, and average pore diameter are compared in these four materials systems.

2. Results and Discussion

Four different stack systems including OSO, NSN, OSN and NSO have been deposited on silicon wafers. The thickness of the silicon film was kept at 25 nm and that of the oxide and nitride barrier layers at 30 nm. These four stacks were then annealed at different temperatures using a rapid thermal processor (fabrication details see Experimental Section).

In the OSO system, nanopores and silicon nanocrystals are formed during rapid thermal annealing and the annealing temperature is a key factor that controls the pore size and porosity. **Figure 1** shows bright field transmission electron microscopy (TEM) images of the OSO system annealed at four different temperatures from 800 °C to 1100 °C. In the bright field TEM images, the pores appear as bright spots while the silicon crystals are in grey or black depending on their crystallographic orientation. Only a few small pores are formed in the silicon film when the annealing temperature is below 1000 °C. The size of these nanopores is around 10 nm in diameter. With increasing annealing temperature, the pores become larger, and reach 30 nm at 1100 °C. Both pore size and porosity increase with the annealing temperature, in agreement with our previous results.

By replacing the top and/or bottom silicon dioxide with silicon nitride, three different stack systems including NSN,
OSN and NSO are explored. Figure 2 shows TEM images of the annealed NSN system at four different temperatures from 800 °C to 1100 °C. This is the first time that pores are reported in ultrathin Si membranes fabricated using another system besides the OSO system. As with the OSO system, the pore size and density in the NSN system increase with the annealing temperature. However, direct comparison of the TEM images shows that the pores are bigger and the pore density is much higher in the NSN system.

Since nanopores can be formed in both the NSN and OSO systems, it is likely that nanopores would be formed in the mixed OSN and NSO systems. In the OSN system the top oxide layer is replaced with nitride while in the NSO system the bottom oxide layer is replaced with nitride. The TEM images of Figure 3 and 4 confirm that nanopores are formed in silicon films after annealing in these mixed systems. Both systems produce a high density of nanopores when the annealing temperature is greater than 1000 °C. They show similarities in the pore evolution with annealing temperature among the four systems. However, the choice of the insulating layers and their deposition order affect the pore characteristics, such as the pore size and pore density.

In order to fully compare the pore characteristics of the four different systems, customized pore recognition software was developed to quantify the pore density, pore size and porosity from the TEM images (available for download at nanomembranes.org/ resources/software, Supporting Information).

Pore density is an important parameter and Figure 5 presents a pore density comparison among the four systems. The pore density in the NSN system, which stays the highest among the four systems for all annealing temperatures, is already high at 800 °C, increases gradually with temperature and appears to saturate at 1000 °C. The pore density in the OSO system, which remains the lowest among the four systems for all annealing temperatures, is very low at 800 °C, changes little until the annealing temperature reaches 1000 °C and increases slightly at 1100 °C. Even at 1100 °C the pore density of the OSO system is 5 to 6 times lower than for the other three systems. The OSN and NSO systems also start with very few pores at 800 °C, however, the pore density increases rapidly as the annealing temperature increases. The pore density of the OSN system exceeds that of the NSO system at 1000 °C and reaches that of the NSN system at 1100 °C. This comparison shows that high density pores can be formed in Si films in the OSN, NSO and NSN systems at high annealing temperature. The pore formation in the Si film is greatly enhanced by the existence of even a single silicon nitride capping layer.

Pore size is another important pore characteristics. Figure 6 compares the average pore diameter (APD) of
the four systems. The differences in the APD among these four systems are not large as for the pore density. The NSN system yields slightly larger APD among four systems when the annealing temperature is below 1000 °C. The APDs in the OSN and NSO systems are smaller than in the NSN system for all temperatures. The APD for the OSO system is the smallest at 800 °C but it increases rapidly, becoming the largest at 1100 °C. This can be understood by plotting the pore distribution. Figure 7 shows the pore distributions of the four systems at 1100 °C. In the OSO system, the pore density is not high but the majority of the pores are from 24nm to 38nm in diameter. In the NSN system, the pore density is much higher than that of the OSO system but the majority of the pores are from 20nm to 30nm in diameter. The pore distributions of the OSN and NSO systems yield slightly smaller pores compared to the NSN system.

Pore distribution plots can also be used to illustrate the pore evolution with annealing temperature. Figure 8 compares the pore distribution of the OSO and NSN systems at four different annealing temperatures. In the OSO system, as the annealing temperature increases, the pore size distribution quickly shifts to larger diameters without significantly increasing the total pore density. This indicates that pore growth rather than new pore formation dominates the pore evolution process in the OSO system. The NSN system, however, shows a different pore evolution. With increasing annealing temperature, the pore distribution slowly shifts to the large pores. At the same time, the density of relatively small pores (<20 nm) remains high. This indicates that new pore formation plays a big role in the pore evolution of the NSN system at higher annealing temperatures.

In addition to the pore density and pore size, porosity is another important characteristics. Figure 9 compares the porosity among the four systems. The NSN system yields the highest porosities at all temperatures. The porosity increases rapidly with the annealing temperature and reaches 20% when the NSN system is annealed at 1100 °C. In contrast, the porosity in the OSO system stays the lowest among the four systems at all annealing temperatures. It increases very slowly when the annealing temperature is below 1000 °C. Even at 1100 °C, the porosity is only 3.8%. The porosities in the OSN and NSO systems start low at 800 °C and increase quickly with annealing temperature. They stay between those of the NSN and OSO systems at all annealing temperatures. Consistent with our previous observation, the large difference in porosity between the NSN and OSO systems is due to the pore density. At higher annealing temperatures, the NSN system produces not only larger but denser pores while only a limited number of larger pores are formed in the OSO system. In other words, pore formation is enhanced in silicon...
films when sandwiched by silicon nitride layers compared to silicon dioxide layers, yielding the highest pore density and porosity. This highly porous Si membrane from the NSN stack is very promising for filtration applications since a large number of relatively big pores would enhance the fluid flow through the membrane.

Figure 4. TEM images of the NSO system after RTP annealing at a) 800 °C, b) 900 °C, c) 1000 °C and d) 1100 °C.

Figure 5. Pore density for the four systems as a function of the annealing temperature. Each number is the average of three results from three different TEM images and the error bar represents the standard deviation.

Figure 6. Average pore diameter (APD) for the four systems as a function of the annealing temperature. The vertical bars represent the middle 50% of the pore size distribution in the OSO system at each temperature. The width of the distributions increases with temperature for all four systems.
In all four systems the pore density, size and porosity increase with the annealing temperature, indicating that nanopore formation is thermally driven and closely related to crystallization in the silicon film. It has been reported that the type of interface would influence the crystallization behavior of amorphous silicon. As the NSN and OSO systems have different interfaces, it is likely that the crystallization of the amorphous silicon films would be affected by different interfaces in these two systems. A possible explanation for the pore formation enhancement in the NSN system might be found in the interface energy difference between silicon/silicon nitride and silicon/silicon dioxide. Indeed, our work has constantly shown that pore formation is associated with Si nanocrystal formation. Further investigation is needed to fully understand the pore formation process in these two different systems.

3. Conclusion

This work reported for the first time that nanopores can be formed in an amorphous silicon film sandwiched by two silicon nitride films during a rapid thermal annealing. This discovery introduces a new control variable for pnc-Si membrane fabrication, demonstrating new properties in the expanded NSN materials system. Four different systems including OSO, NSN, OSN and NSO have been tested. It was found that the NSN system produces the highest porosity and pore density after annealing, while the OSO system produces the lowest. The porosity and pore density of the mixed OSN and NSO systems fall between those with matched barrier.
4. Experimental Section

Fabrication of pnc-Si membranes involves a bottom-up approach. First, the backside of (100) N-type silicon wafers with 100 nm thick thermal oxide are patterned using standard photolithography technique. Then four different stacks, including the NSN, OSN, NSO, and ONS, are deposited on the front side of the patterned wafers using rf-magnetron sputtering (ATC-2000 V, AJA International, Inc., North Scituate, MA) respectively. Each stack is a three-layer structure. The thickness of the silicon film is kept at 25 nm and that of the nitride and oxide films at 30 nm. The deposition temperature is 150 °C for all films and the deposition pressure is 3mTorr for the amorphous Si and 5 mTorr for the oxide and nitride. Amorphous silicon is deposited under a 5 W bias while silicon dioxide and silicon nitride are deposited under a 50W bias.

After deposition the wafers are etched from the patterned side using a customized single-side Si etch cell with a wet anisotropic etchant, ethylene diamine pyrocatechol with pyrazine (EDP-300F, Transene Company Inc., Danvers, MA) at 110 °C. The bottom silicon nitride or silicon dioxide works as an etch stop because EDP has very high silicon-to-oxide and silicon-to-nitride etch ratios. A rapid thermal processor (RTP) is then used to induce solid phase crystallization (SPC) of the amorphous silicon layer (Solaris 150, Surface Science Integration, El Mirage, AZ). Samples are annealed at different temperatures ranging from 800 °C to 900 °C, 1000 °C, and 1100 °C respectively. The annealing process involves a fast ramp up rate of 50°C/s and a soaking time of 1 minute at the set temperature. Samples are placed inside a silicon carbide coated graphite susceptor to improve heating uniformity. We did not explore higher annealing temperatures because delamination of the films was observed after annealing at 1200 °C. The protective silicon nitride and silicon dioxide film are removed using HF after annealing. Figure 10 illustrates the process for the NSN system.

After removal of the silicon substrate and the protective layers, the free-standing pnc-Si membranes were characterized using a Hitachi 7650 transmission electron microscope (TEM) operating at 100 kV. The pnc-Si membranes were patterned to be compatible with the TEM specimen holder. Because the thickness of the membranes was only 25 nm, no additional sample preparation was required. Images were acquired with an Olympus Cantega 11 megapixel digital camera.


