Simulation of Nanochannel Membrane Formation

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Abstract—Monte Carlo simulations of atomic processes on the surface of silicon nanochannel membranes during molecular-beam epitaxy and subsequent thermal oxidation are performed. It is demonstrated that silicon deposition on Si(001) wafers with 1–100 nm cylindrical pores results in constriction of channel inlets. The rates of reduction of the nanochannel diameter are estimated as functions of the wafer temperature, silicon deposition rate, and initial nanochannel diameter. Optimal conditions of silicon deposition on nanochannel membranes are determined: the wafer temperature of 250–450°C and silicon flux intensity of $10^{-2}$ to 10 monolayers (ML) per second. Under these conditions, the rate of reduction of the nanochannel inlet diameter is 0.13–0.15 nm/ML, which allows membrane channel modifications over a wide range down to several nanometers. Simulations of nanochannel membrane oxidation in an oxygen flux shows that precise reduction of nanochannel inlet diameters down to complete sealing of the channel due to oxide growth is only possible for small diameters of the initial pores. For channels with large lateral sizes, the effect of reduction of the channel inlet diameter due to oxidation is insignificant. Oxidation of pores enhances their stability to subsequent high-temperature treatment.

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INTRODUCTION

The interest in membrane technologies aimed at mass sequencing of nucleic acids and separation, concentration, and transportation of biomaterials is caused by their possible applications in medicine and biology. The following membrane technologies designed for ultrafine filtration of colloid and biological solutions should be noted: track-etched polymer membranes [1], which cover the range of 20 to 1000 nm, submicron membranes made of ordered Al$_2$O$_3$ structures [2] and of self-organizing ensembles of SiO$_2$ nanoparticles [3, 4], and membranes made of carbon nanotubes 1.3–2.0 nm in diameter located on silicon chips [5]. Si-based nanochannel membranes inspire the greatest interest [6–9], because they offer much promise in terms of unification into a final device at the modern level of microelectronics. The transverse size of nanochannels in multichannel Si-based membranes fabricated by methods of electrochemistry [6] and crystallization [7] was 9 to 30 nm. Small nanochannels (1.8 and 1.0 nm) were obtained for single-channel membranes [8, 9], but such membranes are designed for analyzing single molecules and cannot be used for ultrafine filtration of colloid and biological solutions. A unified approach to fabrication of nanochannel membranes in the entire nanometer range from 1 to 100 nm is currently unavailable. Attempts were made to solve this problem on the basis of semiconductor silicon and silicon dioxide by a technology where nanochannel membranes are formed on the basis of meso- and macroporous silicon [10]. Porous silicon is obtained by means of anode electrochemical etching of hole-type monocrystalline silicon possessing a capillary structure of pores whose sizes vary from several nanometers to tens of micrometers. Electron-beam lithography and plasma-enhanced chemical etching allow obtaining membranes with ordered nanochannels in a topology of 30–100 nm. These technologies, however, have physical constraints for the range of 1 to 30 nm. Additional processes that make it possible to reduce the sizes of nanochannels obtained with a topology of 30–100 nm are proposed to
obtain nanochannel membranes with channel diameters of 1 to 30 nm. These processes are molecular-beam deposition of silicon on a silicon membrane and thermal oxidation.

In the activities described in the present paper, we performed a numerical experiment on transformation of a complicated surface of a silicon nanochannel membrane during molecular-beam deposition silicon and subsequent thermal oxidation in an oxygen flux by means of Monte Carlo (MC) simulations. The idea of these simulations was to estimate the scale of possible modifications and to obtain some preliminary quantitative dependences between the process parameters and structural characteristics of the membrane prior to experimental investigations of this complicated object. The effectiveness of Monte Carlo simulations was demonstrated in studying the processes of sealing, sintering, and annealing of porous structures on Si(001) and Si(111) wafers [11–13]. An upgraded MC model was used in the present computational experiment with nanochannel membranes; this model allowed us to consider a multispecies system with reactions between elements of different chemical nature.

1. COMPUTATIONAL MODEL

The computations were performed by the SilSim3D software system, which is briefly described in [14,15]. The SilSim3D software system was developed for simulating a number of key technological processes in microelectronics, such as annealing, molecular-beam epitaxy, and chemical vapor deposition. SilSim3D allows systems containing up to seven species of different chemical nature to be considered. The software system is based on a lattice model of solid layers, which allows MC simulations of systems up to several hundreds of nanometers in size. The time needed for process simulations is commensurable with the time needed for a physical experiment. An elementary event in the model was compared with a certain probability of this event. The event probability \( P \) was determined by its activation energy \( E_a \): \( P = \nu \exp(-E_a/k_BT) \), where \( \nu \) is the Debye frequency \( (\approx 10^{13} \text{ s}^{-1}) \), \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature. The activation energies of various events were the input parameters of the model. The following elementary events were considered in the model system:

1. diffusion jump of an atom to free nodes of the lattice in the first three coordination spheres;
2. absorption of an atom on the open surface;
3. desorption of an atom from the open surface;
4. evaporation with subsequent reabsorption of particles in closed cavities;
5. chemical transformations of particles of one species to another.

An arbitrary number of single-species and two-species chemical reactions between particles in the subsurface layer could be specified.

For simulating the process of molecular-beam deposition of silicon onto the surface of the nanochannel membrane, we chose a wafer with a diamond-type lattice with the surface orientation (001) and with vertically aligned cylindrical channels. The flux of silicon atoms was directed normal to the wafer. In simulations of sealing of large-diameter nanochannels \( (d_0 > 20 \text{ nm}) \), the following procedure was used to reduce the number of lattice sites considered and, as a consequence, the computer memory requirements. The model system was assumed to have two species, i.e., to consist of the upper layer simulating silicon and the lower layer acting as an absorber of any substance arriving from outside, which allowed us to simulate sealing of a porous wafer with channels of unlimited length. The transition to a multispecies system made it possible to simulate sealing of large-diameter pores with the model system size within \( 10^7 \) atomic sites. The deposition rate \( V \) was varied in the computations from \( 10^{-3} \) to \( 10 \text{ ML/s} \), and the wafer temperature was varied from 230 to 730°C.

Silicon oxidation simulations were based on the concepts developed in [16], which imply that the structure of amorphous SiO₂ with correct coordination of silicon and oxygen atoms can be obtained on a partly filled diamond-type lattice. The model of silicon dioxide growth was first tested on examples of oxidation of Si(001) and Si(111) flat surfaces in an oxygen flux at temperatures of 500 to 1100°C and pressures of \( 10^{-4} \) to \( 10^{-2} \text{ torr} \). The parameters found in [17] were used in computational experiments on oxidation of silicon-based nanochannel membranes.

In oxidation simulations, oxygen molecules were incident onto the membrane from the gas phase at a random angle, which offered access to all elements of the complicated surface; these molecules could evaporate from this surface at an arbitrary angle as well. For this reason, oxygen molecules were allowed to make multiple attempts to deposit onto the channel walls. Oxidation was simulated in a system of four species: Si, O₂, O, and SiO. On the membrane surface, an oxygen molecule participated in a reaction with a silicon atom. As a result, atomic oxygen and silicon monoxide were formed. The latter, in turn, could