INITIAL STAGES OF SILICON GROWTH ON THE (100) SURFACE OF SILICON BY LOCALIZED LASER CVD

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ABSTRACT

This paper reports initial results of an experimental study of the early stages of silicon thin film growth on well prepared (100) c-Si surfaces by pyrolytic deposition from silane (SiH_4) during localized laser chemical vapor deposition (LLCVD). The rate of silicon thin film growth during low pressure (< 10 Torr) deposition using tightly focussed laser beams (514.5 nm, ~ 2.5 μm FWHM) is characterized and is shown to be much slower than expected based on the previously measured silane decomposition rate. Hybrid–heating experiments, in which laser heating induces a slight temperature increase on a uniformly heated substrate in the presence of silane gas, shows that growth is inhibited within the laser irradiation region. This result suggests that a nonpyrolytic mechanism contributes to silicon growth in laser CVD. Possible explanations for this nonpyrolytic growth mechanism are discussed.

INTRODUCTION

Localized laser chemical vapor deposition (LLCVD) is an important process for the direct generation of thin films with micron dimensional spatial features, which is finding novel applications in microelectronic processing [1,2]. The purpose of this investigation is to probe the growth mechanisms and kinetics which are important in the initial stages of silicon thin film deposition during pyrolytic decomposition from silane (SiH_4) by LLCVD. This phase of thin film deposition plays a crucial role in determining interface and thin film properties, and can influence reproducibility of deposit formation during LLCVD.

The process of nonepitaxial, three–dimensional island, thin film growth can be divided into three distinct steps: the nucleation phase, where a supersaturated concentration of adatoms combine to form critical nuclei which have a greater probability of growing than decaying; the coalescence stage, where critical nuclei grow together producing a contiguous thin film of material; and the continued growth stage, where material is deposited onto the already deposited film. The effects of the nucleation phase have been shown to be important during LLCVD [3]. Several authors have reported difficulty depositing material onto a bare substrate surface, but noticed that it became relatively easy to grow thin film microstructures onto already nucleated areas of the surface.

The dynamics of nucleation during LLCVD have been modeled recently [4,5]. Nucleation was shown to influence the initial thin film morphology. Results from a Monte Carlo simulation of nucleation [5] show that at a given pressure of parent molecules and adsorbate–substrate binding energy, there is a critical temperature T_c such that for laser–induced peak temperatures $T_p > T_c$, nucleation will occur initially in an annulus region centered with respect to the incident laser beam. While, for $T_p < T_c$, most of the initial material will form at the center of the laser heated region forming disk–like deposits. For LLCVD of silicon on c–Si, these disk–like deposits are expected to form. This simulation included only conventional CVD steps, was conducted for LLCVD of silicon and incorporated the silane decomposition studies of Farrow [6].

Here, the rate of polysilicon deposition by low pressure LLCVD (514.5 nm, 2.5 μm FWHM)

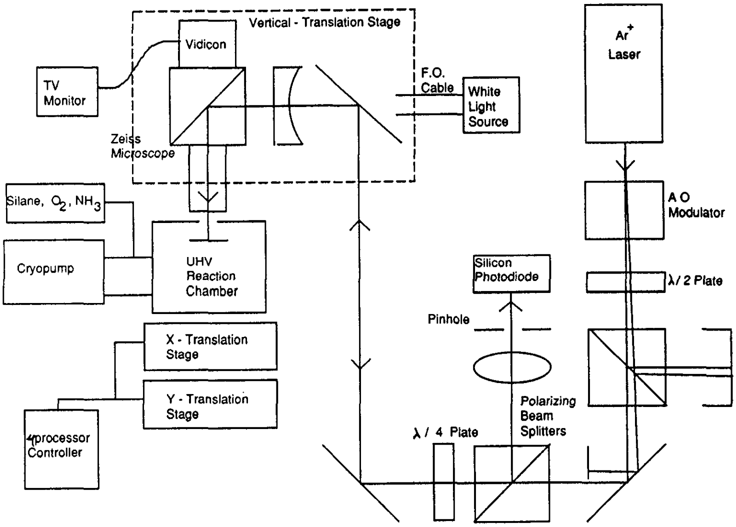

Figure 1: Schematic diagram of the experimental apparatus.

from silane (< 10 Torr) on well prepared (100) c-Si surfaces is characterized. The measured growth rate is less than that expected based on model calculation. Discrepancies between expected and measured growth rates are further investigated using hybrid–heating experiments where both laser heating and thermal conduction heating are used simultaneously to deposit a thin film of silicon.

EXPERIMENTAL TECHNIQUE

A schematic diagram of the experimental arrangement is shown in Figure 1. The sample under study is situated horizontally in an UHV reaction chamber, with the laser incident in the vertical direction through an optical window at the top of the chamber. The stainless steel reaction chamber used for the experiments contains all metal seals, is bakeable to 400°C, and contains provisions for heating and measuring the sample substrate to temperatures of 1200°C. The window assembly is attached to a welded bellows to facilitate placement of the window in close proximity (~ 2 mm) to the sample for deposition experiments or far from the sample (50 mm) to prevent window damage during substrate preparation by heating. Sorption pumping and cryo pumping are used exclusively to reduce the pressure in the vessel to a base value of $\sim 5 \times 10^{-10}$ Torr.

The output duration of a cw Ar^+ laser (514.5 nm) is adjusted by a quartz crystal acousto–optic deflector. The beam is steered into a modified laser microscope which focuses the light onto the sample surface. The distance between the microscope/focusing objective and the sample surface is controlled by a high precision (0.1 μm positional accuracy) translation stage. By analyzing the shape of the reflected beam from the surface, a constant laser spot size is maintained at the surface. A vidicon camera allows monitoring of the sample surface during deposition.

Surface preparation is vital when studying the nucleation and early growth phases of thin film growth. Both impurities adsorbed onto the surface as well as surface structure defects can

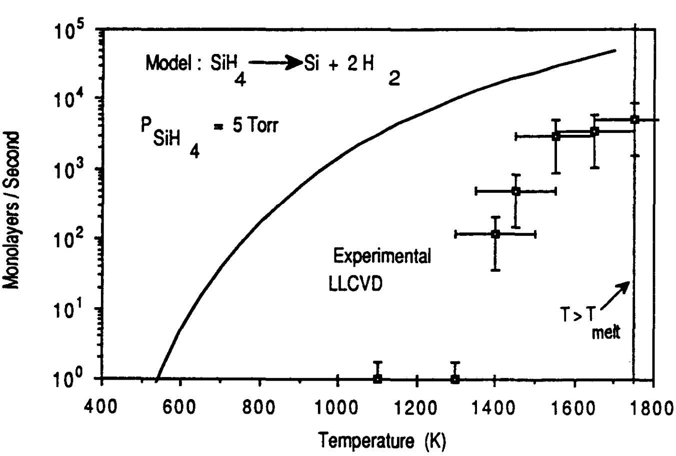

Figure 2: Expected silicon growth rate as a function of temperature using the silane decomposition rate constant by Farrow [6] in the model of reference [5], and the measured deposition rate of silicon on the (100) silicon surface during low pressure laser CVD.

alter the initial thin film formation. Commercially available, polished, silicon wafers, (100) orientation, 5 – 10 Ω–cm, n–type, are used for the experiments reported here. The silicon wafers are scribed into 5 mm squares and cleaned using the RCA procedure [7,8], and immediately loaded into the reaction chamber. After chamber bakeout and pump down to a base pressure of $\sim 5 \times 10^{-10}$ Torr, the silicon sample is *in situ* cleaned by flash heating to ~ 1000°C in ultrahigh vacuum. Auger analysis performed by others [8] and independently confirmed here in another vacuum system, shows that the flash heating removes the native oxide and produces a clean silicon surface. The silane gas with an effective resistivity of > 500 Ω–cm is used as provided, with no additional purification.

EXPERIMENTAL RESULTS

The expected and measured growth rate of silicon deposition on the (100) silicon surface by low pressure laser CVD is shown in Figure 2. The silane pressure was 5 Torr so that the mean free path in the gas phase is greater than the laser spot size at the surface (2.5 μm FWHM). This low pressure regime offers two simplifications to understanding the growth dynamics. First, the transport of gas to and from the surface is governed by molecular flow and hence the rate of incident silane molecules to the surface is accurately determined. Second, the number of gas phase collisions between thermally excited molecules is limited, thus inhibiting homogeneous decomposition of silane in the gas phase. The surface decomposition rate of silane has been measured previously by Farrow [6] and the expected growth rate based on his results is shown by the solid line in Figure 2. To plot the experimental growth rates, the laser spot size at the surface was accurately measured (2.5 μm FWHM) and the laser induced temperature profile was computed using a finite difference solution to the thermal diffusion equation. Since the optical and thermal properties of silicon are well known, the surface temperature distribution can be determined to an accuracy of ±100° C. The experimentally determined growth rate was obtained by dividing the thickness of material deposited within the central 1 micron region of the disk-like deposit by the duration of the laser pulse, and plotting this at the average temperature over the central 1 micron region (which differed from the peak temperature by < 100° C for the 2.5 μm FWHM laser spot size).

As can be seen from Figure 2, the experimentally determined growth rate is considerably less than the expected growth rate based on the decomposition data of Farrow. It should be noted that this discrepancy is especially significant at temperatures < 1300 K where the measured growth rate is more than 4 orders of magnitude slower than that expected.

In order to resolve this discrepancy, hybrid-heating experiments were performed in which both laser heating and conduction heating were used simultaneously in order to compare the relative rates of thin film growth during LLCVD with conventional CVD. Once silane gas was added to the reaction vessel, the temperature of the silicon substrate was raised to 600 – 800 K so that a silicon thin film was deposited very slowly over the entire substrate surface and laser light was simultaneously focussed to a spot size of ~ 200 μm FWHM at the sample surface to induce a slight surface temperature rise over the irradiation region. Figure 3 shows a schematic representation of the hybrid-heating experiment. Due to the low surface temperatures, decomposition kinetics are still surface dominated. Starvation of silane molecules by gas phase diffusion should not affect the resulting thin film. This is proven by the fact that a uniform thin film is deposited over the entire substrate surface when only thermal conduction heating is used. Since the deposition rate of silicon is known to increase monotonically with temperature, one would expect to find a rather uniform thin film deposited over the entire surface with a greater thickness of material deposited on the laser irradiated region (by a factor of 2 for the experimental conditions examined) where the temperature is a maximum, as is shown in the figure.

A typical result of a hybrid-heating experiment is shown by the scanning electron micrographs of Figure 4. The uniform surface temperature was ~ 650 K, the laser power was 3.8 W, the spot size at the surface was ~ 200 μm FWHM and the silane pressure was 6 Torr. The temperature rise $\Delta T_{\mathrm{Laser}}$ induced by the laser irradiation was calculated to be ~ 55 K under these conditions. The surprising result, which can be seen in the figure, is that less material was deposited within the laser irradiation region (the 300 μm diameter dark region in the left photograph of figure 4) than at other locations of the thermally heated surface, completely opposite of what would be expected. Note the large granular morphology which appears only in regions of the surface away from the incident laser irradiation. Thin film growth inhibition within the laser irradiated region of the surface is very reproducible in hybrid-heating experiments.

DISCUSSION

The hybrid-heating result suggests that a nonpyrolytic, non-CVD mechanism plays a part in the growth of silicon thin films by LLCVD from silane on (100) silicon. This photon-induced non-CVD mechanism suppresses the rate of thin film growth relative to that which occurs during purely thermal deposition. This effect is believed to be responsible for the discrepancy shown in Figure 2 between the measured silicon growth rate during LLCVD and that predicted from purely thermal growth conditions.

To explain the reduction in the silicon growth rate within the laser irradiation region during the hybrid-heating experiments, the differences between low pressure conventional CVD by thermal conduction heating and localized laser CVD need to be addressed. In general, there are three fundamental differences which need to be explored. First, in laser CVD, the deposited thin film material is localized to spatial dimensions with a lateral extent of < 400 μm. Because a silane molecule, the SiH_2 radical, or a silicon atom migrates an average distance of only a ~ 100 Å on the surface before either desorbing back into the gas phase or becoming incorporated into the lattice, material localization to dimensions > 1 μm should not affect the growth dynamics.

In addition to the deposit localization, two nonthermal effects present in LLCVD might possibly alter thin film growth dynamics: a direct photon-adsorbate interaction, which could lead

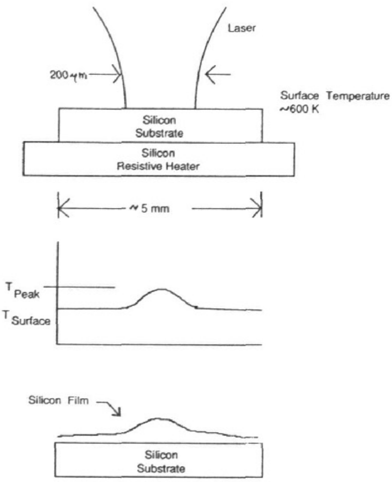

Figure 3: Schematic representation of hybrid–heating experiment. The bottom figure shows the expected profile of the deposited thin film based solely on thermal growth mechanisms.

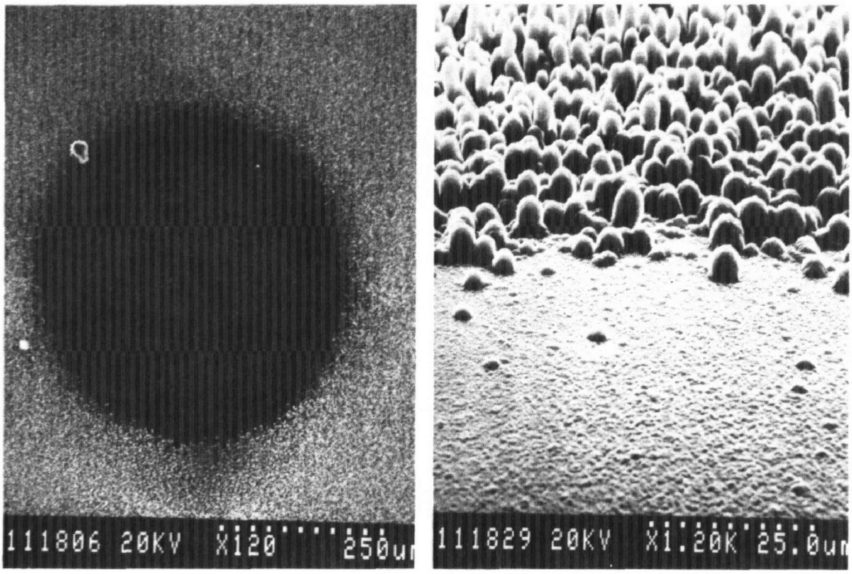

Figure 4: Scanning electron micrographs of silicon deposition from silane by hybrid–heating with a silane pressure of 6 Torr, a surface temperature $T_{\text{surf}} = 650$ K, a laser power of 3.8 W, and beam spot size of 200 μm FWHM. The dark circular region (~ 300 μm diameter) in the left photograph is centered with respect to the incident laser irradiation. The right photograph shows an expanded view of the region where purely thermal growth (upper region) separates laser inhibited growth (lower region).

to photodesorption or enhanced migration of either silane molecules, intermediate radicals, or silicon deposit atoms; and a photoexcited electron–hole pair interaction with an adsorbed species, which could lead to increased adsorption of H or H_2 (thus poisoning surface sites), the inhibition of silane dissociation on the surface, or increased desorption or migration of silane molecules, intermediate radicals, or deposit atoms. Calculations show that for typical deposition conditions used during LLCVD with both $\sim 1\ \mu m$ and $\sim 200\ \mu m$ laser spot sizes, the rate at which photons are incident per atomic site per second at the surface is greater than the rate of incidence of silane molecules per site per second for silane pressures in the few Torr range. Thus, a direct photon–adsorbate atom interaction cannot be ruled out based on simple number arguments. Furthermore, by equating the rate of photoexcited electron–hole pair creation ($\frac{I}{h\nu}$ where I is the intensity and $h\nu$ is the photon energy) with the rate of decay by Auger recombination, the steady–state electron–hole pair concentration in silicon is found to exceed that produced during conduction heating by a factor of 10 to 10^7 for typical conditions encountered during LLCVD.

At present, the exact fundamental mechanism which causes the reduction in the silicon growth rate when a flux of photons is incident is not known. Further characterization of silicon deposition onto silicon, as well as onto thin films of SiO_2 and Si_xN_y, are in progress to understand this phenomenon better . A more detailed characterization of this seemingly nonpyrolytic mechanism occurring during LLCVD of silicon from silane will be given elsewhere.

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