INFLUENCE OF TEMPERATURE ON THE DEPOSITION RATE OF POLYCRYSTALLINE SILICON OBTAINED BY VERTICAL LPCVD

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ABSTRACT

Since the first use of Polycrystalline Silicon (poly-Si) in the semiconductor industry in the middle 70's, it became a material of major importance for micro fabricated devices. In the recent area of Micro-Electro-Mechanical Systems (MEMS), the poly-Si has also been shown to be of great importance and usefulness. The use of MEMS devices normally requires thick layers to be concluded (>1 μ m), so that, high deposition rates are necessary. In this paper we study the influence of Temperature in the deposition rate of a LPCVD Vertical Reactor installed in the Center for Semiconductors Components (CCS) of the University of Campinas (UNICAMP). The activation energy and temperature influence on the deposition rate are analysed using an Arrhenius equation.

1. INTRODUCTION

Polycrystalline Silicon (poly-Si) has been widely used in different microelectronics devices since the 70's. More recently, MEMS (Micro Electro Mechanical Systems) devices have been studied using Poly-Si. This kind of device use thick layers (> 1 μ m typically) of Poly-Si to be built so high deposition rates are necessary to obtain these films in a relatively short times [1]. In this work we use an Arrhenius dependence ($\alpha \exp(-Ea/kT)$) to analyze the influence of temperature on the deposition rate and kinetics of the Poly-Si on thermically oxidized silicon substrates. This study is part of the final characterization of the PMC200 Pancake Vertical CVD Reactor recently installed in CCS/UNICAMP and adapted for the LPCVD process.

2. EXPERIMENTAL PROCEDURES

Thin films of Poly-Si were deposited by LPCVD in a Pancake Vertical Reactor on 0,6 μ m thermally oxidized <100>, n-type, 1-10 Ω .cm single crystalline silicon substrates. The reaction atmosphere was Silane diluted in Hydrogen (flow rates of 40 sccm and 4800 sccm, respectively). We analyzed the deposition rate in the temperature range (measured with an infrared pyrometer) from 700 to 900 °C at 50 °C steps for the pressures of 5 or 10 Torr. Schematic of the LPCVD apparatus is shown in Figure 1.

Film thickness was obtained using a DEKTAK 3 scan profiler in steps built by wet etch of the Poly-Si samples in a $HNO_3: H_20: HF$ solution (50 : 20 : 1). This etch solution is very selective with thermal oxide (< 8 nm/min).

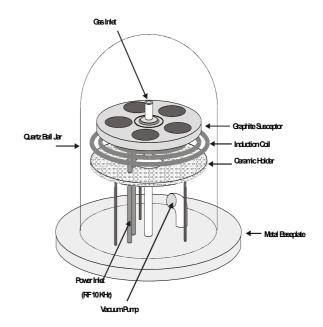


Figure 1 - Schematics of the PMC200 LPCVD Pancake Vertical Reactor.

3. RESULTS AND DISCUSSIONS

We observed that the deposition rate of the Poly-Si has strong influence of the temperature varying from 16 to 1500 Å/min at the 5 Torr samples and from 75 to 2000 Å/min at the 10 Torr samples (Figure 1). Ones can also notice from Figure 1 that increasing temperature from 850 to 900 °C leads to a less change in the deposition rate. Thickness uniformity was below 2 % in all samples.

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The rapid variation of the deposition rate below 850 °C indicates that the deposition process is limited by reaction rate of the silicon precursors at the surface of the substrate (reaction-rate limited) [2]. In this regime, the deposition is an activated process and it obeys the Arrhenius equation as presented below:

$$R_{\rm D} = A + B \exp\left(-E_{\rm a}/kT\right) \tag{1}$$

where R_D is the deposition rate in Å/min, k is the Boltzman's constant, T is the absolute temperature, A and B are fitting parameters and E_a is the activation energy. For the range from 700 to 850 °C we found activation energy of 2,55 and 1,86 eV (59 and 43 Kcal/mol) for 5 and 10 Torr respectively, which are in agreement with historical data [2-3]. The correlation coefficient for both fit are > 0,999.

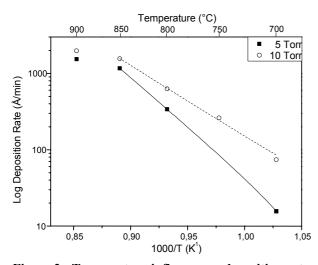


Figure 2 - Temperature influence on deposition rate

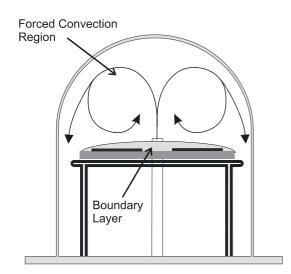


Figure 3 - Simplified schematics of the PMC200 showing the boundary layer and forced convection region.

In the deposition process, the silicon precursors species reach the substrate surface from the forced convection region through the Boundary Layer (Figure 3). The boundary layer is a low velocity region just above the samples and substrate where atoms migrate by diffusion process, equation 2:

$$F_1 = D \frac{(C_G - C_S)}{\delta} \tag{2}$$

- F_1 = Flow rate though boundary layer
- h_G = Gas diffusion coefficient of the reactant gas in the boundary layer
- C_G = precursor species concentration in the forced region
- C_s = precursor species concentration on the sample surface
- δ = boundary layer thickness

i.e., diffusion occurs due to a concentration gradient and not due to a pressure gradient (characteristic of the forced convection region). There are two flows within the boundary layer: precursor species diffuse from the convection region to samples surface and the byproducts diffuse in the opposite direction [2]. From now on we'll consider just the precursor species diffusion and admit that byproducts are fully removed from the system.

Since the forced convection region is plenty of precursor species for the poly-Si deposition, the diffusion rate F_1 thought the boundary layer will depend initially on the species concentration on the sample surface C_8 (Figure 4).

Once in the sample surface, the precursors will be adsorbed and reacted to deposit the solid thin film according to equation 3:

$$F_2 = \kappa (C_S - C_{eq}) \tag{3}$$

 F_2 = reaction rate at surface

- C_s = precursor species concentration on the sample surface
- C_{eq} = gas concentration in equilibrium with the solid
- κ = reaction-rate coefficient

The coefficient κ is an exponential function of temperature. In a steady state condition, both flux rates will be equal and the lower value will limit the overall CVD process.

For 700 °C deposition process, we found that the reaction rate coefficient κ is of low value, due to this temperature dependence. This means that not all precursors that reach the surface reacts to form the solid thin film and the overall process is limited by the reaction rate of the precursor species in the sample surface. With a low reaction rate, C_s will become higher and the diffusion F₁ through the boundary layer will reduce leading to a low deposition rate. Raising temperature process the precursors will react more rapidly and we'll find exponentially higher deposition rates in an Arrhenius form due to the temperature influence on the κ value. Far all this the deposition process is called a Surface-Reaction-Rate Limited.

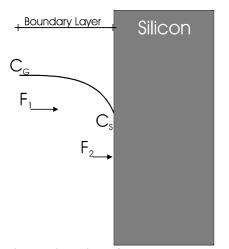


Figure 4 - Detailed view of the boundary layer [4].

Raising C_G (higher pressure) will lead to a higher C_S and to a higher deposition rate as seen in Figure 2, but pressure influence is not as strong as temperature.

At temperatures higher than 850 °C, we found the Arrhenius equation not to rule the process anymore. This is because at elevated temperatures, the reaction is so fast (κ becomes so high) that all precursor atom/molecule reaching the surface is immediately reacted to form the solid film. This condition implies in high diffusion rate F₁ to support the exponential dependence to continue, but F₁ depends on C_G value and cannot raise more than a limit. Reaching this point, the deposition rate we'll be limited by the amount of the precursor species in the forced convection region and the process is called Mass-Transport Limited.

4. CONCLUSIONS

In this paper we studied temperature influence on the deposition rate in the PMC200 Pancake Vertical LPCVD Reactor installed in the CCS/UNICAMP using Hydrogen diluted Silane atmosphere. In the temperature range from 700 to 850 °C, we found the deposition to be an activated process with activation energy of 2,85 and 1,86 eV for 5 and 10 Torr deposition pressure respectively. The correlation coefficient for an Arrhenius like (exponential) fit is > 0,999 for both applied pressure. In this temperature range the deposition process is in the Reaction-Rate limited regime.

Above 850 °C, we observe a deflection from the exponential indicating another limitation step. In the high temperature deposition the process is in the Mass Transport Limited regime.

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