Deposition Mechanism of Direct-Write Processes – An Application-Oriented Approach to Custom-Tailored Material Properties

H.D. Wanzenboeck, S. Harasek, H. Langfischer, E. Bertagnolli

Institute for Solid State Electronics, Vienna University of Technology

Chemical vapor deposition (CVD) utilizes the adsorption and decomposition of a volatile gaseous species on a sample surface. For coating of large areas thermal CVD or plasma enhanced CVD has been established as versatile deposition technique for dielectrics and metals. In contrast to large area coating techniques, a local direct-write technique is introduced using a focused energetic beam to provide the necessary activation energy for CVD. With a focused ion beam, material has been locally deposited within a strictly confined area down to the nanometer range. For this direct-write nanodeposition of silicon oxide, two precursor gases – siloxane and oxygen – have to be added simultaneously. For this local CVD process, an exposure by a scanning beam (FIB) followed by a waiting time allowing for new re-adsorption of the precursor is required. An influence of the different ion exposure times per scan and an effect of the mixture ratio of precursors in the gas phase have been observed. The chemical composition of the solid silicon oxide and the physical properties can be tailored to demand by deliberate changes of process parameters. The beneficial aspects of the process versatility are demonstrated by deposition of insulating layers, structures with smooth surfaces, and 3-dimensional structures.

Introduction

Chemical vapor deposition (CVD) has become extremely popular in microelectronic manufacturing. Due to the versatility of the process CVD is the preferred deposition technique for a wide range of materials – especially for dielectric compound materials. [1]. The requirement for specific shapes of dielectric material in specific functional units has led to the fact that structuring the layer fabricated by CVD is as crucial as the deposition process itself. Multiple process steps including optical lithography followed by chemical etching are the predominantly used approach for structuring. Not only that etching raises the critical issues of material selectivity and etch stop layers, the lithographic approach requiring a specific photomask for every design is very inflexible and time consuming before the first device can be produced. For mass production, the lithographic approach remains unmatched in high throughput and economical value. For rapid prototyping and for 3-dimensional devices an alternative strategy has been sought for a long time.

Recently, direct-write processes utilizing a focused beam of ions, photons or electrons have shifted in the focus of increased interest, as they combine deposition and patterning in a single step [2]. A local gas atmosphere is maintained by introducing the precursor components via a micro-nozzle system [3]. The reaction energy is brought in by energetic ions so that the deposition only occurs in the confined area where the incident ions strike the sample surface [4]. In contrast to large area CVD that needs subsequent lithographic structuring, FIB-CVD allows depositing material while simultaneously obtaining the required structures [5], [6]. This sophisticated technique finally closes the long endured gap between the demand for high-qualitative dielectric material on one hand and a quick prototyping technique for device development on the other hand.

However, the multitude of process parameters with FIB-CVD does not allow a straightforward control of the deposition process, but requires extensive knowledge of the process and the chemical reaction. In this study, both the chemical parameters such as gas phase composition and the beam-related parameters such as pixel spacing have been investigated. The gained process knowledge allows selecting in advance material quality, the deposition rate, and the surface roughness of the deposited layers. An optimum process range has been identified yielding silicon oxide with low contamination and high electrical resistivity [7]. This technique will facilitate the application for fabrication of nanostructured materials in micromachining, MEMS, and for modification of interconnects of microelectronic circuits [8] – [10].

Experimental

Focused beam induced CVD utilizes a focused ion beam with a spot size in the nm regime to initiate the deposition reaction on an arbitrary surface. This maskless direct-write technology facilitates the additive fabrication of dielectric material and structuring towards functional units within a single process step. By guiding the scanned beam, the CVD can be used to deposit pattern designs. Due to the small spot diameter, material deposition can be restricted to the nanometer range so that 3-dimensional nanostructures can be fabricated.

A gas mixture of siloxane (tetramethylcyclotetrasiloxane) and oxygen has been used as chemical precursors to facilitate the deposition of silicon oxide. A focused ion beam of Ga^+ ions has been employed to induce the chemical reaction of the components adsorbed on the substrate surface. As the maintenance of a focused particle beam requires vacuum condition (base pressure 10^{-6} mbar), the chemical precursor compounds were introduced via a micro-nozzle system positioned in close vicinity to the deposition area. The co-adsorbed components are decomposed under formation of silicon oxide by the secondary ions and secondary electrons generated by the impact of the 50 kV Ga^+ ions.

The visual inspection of the deposited structures was performed *in situ* by FIB-imaging recording the secondary electron signal during the beam scan. For purposes of illustration of 3-dimensional structures, the sample surface was tilted during imaging to yield an advantageous view angle. Deposited pads (100 x 100 µm) were used for chemical characterization of the material by secondary ion mass spectroscopy (SIMS) and by Auger electron spectroscopy. The sample surface was pre-cleaned by *in situ* ion milling to remove adsorbed surface species. The characterization of the surface roughness was determined by high resolution transmission electron microscopy (HRTEM) imaging of cross-sections of the deposited layers or by atomic force microscopy (AFM) using tapping mode scans.

Results

With direct-write deposition techniques, arbitrary structures were grown by defining the scan area of the focused beam with a pattern generator. Three-dimensional structures and large layers covering areas up to 1 x 1 µm were deposited without stitching. The dwell time of the beam on a single pixel of the scan was kept short enough to provide a sufficient surface adsorption of precursor for the deposition process. A long exposure of a single spot leads to complete consumption of the adsorbed precursor. This results in increased ion milling and high contamination by Ga and C. The control of the scan area and the scan parameters were shown to be suitable parameters for the custom tailoring of structural features and the surface topology.

Custom-tailoring of structural features

The repetition of the exposure with the energetic beam primarily defines the thickness of the deposited layer. The chemical reaction to deposit material locally is triggered by the energy of the focused energetic beam. By restricting the exposure area on a 2 x 2 µm area and choosing a high repetition of the exposures, pillars with a high aspect ratio of 15:1 could be fabricated (Fig. 1) The efficiency of the deposition was found to depend on the dwell time per exposure cycle and the pixel spacing. By tilting the surface plane during deposition, inclined structures could be deposited (Fig. 1).

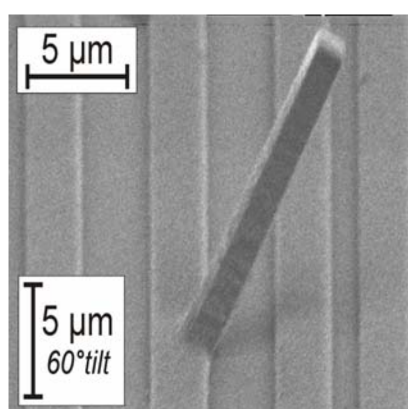

Fig. 1. FIB-deposited 2 x 2 µm pillar made of dielectric material with a total height of 30 µm total. The pillar is deposited with a controlled 30° tilt to the sample surface.

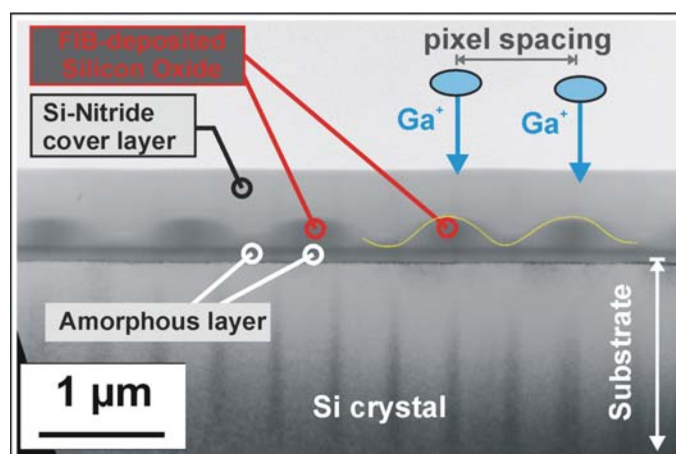

Fig. 2. TEM - cross section (left) Silicon oxide was deposited with a 1 µm pixel spacing of a 300 nm beam. A pattern of deposited bumps was obtained allowing to generate a predefined surface roughness.

In previous studies, the influence of the pixel spacing on the chemical composition of the deposited silicon oxide was confirmed. By choosing a large pixel spacing exceeding the diameter of the focused beam also the morphology can be influenced deliberately. By adjusting the pixel spacing during the deposition scans larger than the beam diameter, an intentional surface roughness can be generated. By depositing silicon oxide with a pixel spacing of 1 µm, a repeated pattern of depositions could be produced. The cross-section of this layer shows distinguishable bumps of silicon oxide

with a periodicity of the pixel spacing and a height of 200 nm (Fig. 2). The FIB-deposited material was covered with a protective layer of silicon nitride to inhibit artifacts during polishing of the ultrathin cross-section for HRTEM-imaging. By adjusting the pixel spacing small enough to produce a beam overlap, smooth surfaces with a RMS roughness of 3.2 nm were obtained according to AFM measurements. However, the deposition efficiency was observed to decrease with narrow pixel spacing. It is assumed that the consumption of precursor in overlapping beam spots exceeds the re-adsorption rate from the gas phase, so that the sufficient precursor coverage is not assured any longer.

Chemical Composition

The gas composition was observed to have a fundamental influence on the deposited material. As mentioned before, refresh times between the single scans were chosen long enough to work under steady-state conditions excluding diffusion-limited kinetics. With two precursor components silicon and oxygen, those substances are undergoing permanent competitive co-adsorption on surface sites. Their mixture ratio in the gas phase and the total gas pressure above the sample is decisive for the adsorption status. The surface concentrations of every precursor species are influencing for the chemical composition of the deposited dielectric (Fig. 3). Using only pure tetramethyl-cyclotetrasiloxane $Si_4O_4C_4H_{16}$, an atomic ratio of Si:O = 1:1 is already given. Adding molecular oxygen O_2 shifts the ratio towards higher oxide contents.

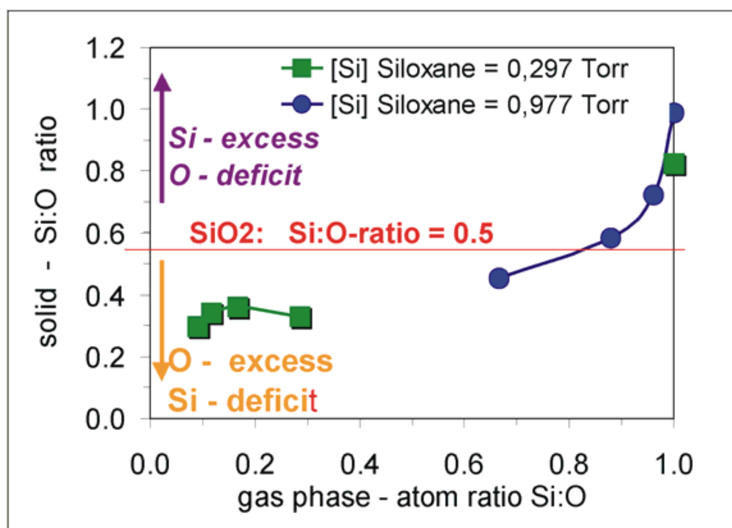

Fig. 3: Si:O atom ratio in deposited solid silicon oxide in correlation to the Si:O atom ratio in the precursor gas mixture. (The siloxane (TMCTS) has a Si:O atom ratio of 1:1. The addition of O_2 changes this ratio.)

The highest purity of deposited silicon oxide could be obtained at a ratio of TMCTS:O_2 = 1:10, reflecting an atomic ratio of Si:O = 1:6. At this mixture ratio, carbon contaminations have dropped below the detection limits of Auger electron spectroscopy, and the Ga implantation is in the range of 10%. In addition, the total pressure of the gas mixture has a significant influence on the deposited material (Fig. 3). A high total pressure was found to be beneficial for the deposition of silicon oxide close to the stoichiometric 1:2 composition of SiO_2. Selecting a precursor gas mixture with a high total pressure and an excess of oxygen, a silicon oxide with low contaminations and a composition close to silicon dioxide was deposited.

Conclusions

Direct-write deposition by a focused energetic beam allows local deposition of dielectric material with a feature size down to the deep sub-μm range. In this work, utilization of a focused ion beam (FIB) for deposition is described as an unorthodox type of chemical vapor deposition (CVD) using the energy of the energetic beam to initiate the chemical reaction only in a confined region.

Experimental results demonstrate the versatility of this method. Direct write deposition allows for custom tailoring of 3-dimensional structures by scanning the beam in a pre-defined pattern. FIB-CVD allows fine-tuning the chemical composition of the deposited material by controlling the gas atmosphere. Furthermore it has been shown that the surface roughness can be modified by deliberate control of the process parameters.

This unmatched flexibility of direct-write deposition of dielectrics bears the potential of becoming a key technology for rapid prototyping of electronic devices as well as for the development of micromechanical systems and for the repair of optical components and photomasks.

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