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Spatial control over atomic layer deposition using microcontact-printed resists

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Abstract

Area-selective thin film growth by atomic layer deposition (ALD) has been achieved on octadecyltrichlorosilane (ODTS) patterned substrates. Patterned hydrophobic self-assembled monolayers (SAMs) were first transferred to silicon and yttria-stabilized zirconia (YSZ) substrates by microcontact printing. Subsequently, films of either HfO_2 or Pt were grown selectively on the SAM-free regions of the surface, while ALD was blocked in regions where ODTS was present. The deposited pattern was readily observed through scanning electron microscopy and scanning Auger imaging, demonstrating that soft lithography is a simple and promising method to achieve area-selective ALD. The selectivity of the soft lithography-based method and the subsequent pattern resolution was compared for Pt versus HfO_2. It was found that using ODTS films, it is easier to achieve complete deactivation of Pt than HfO_2.

Keywords: Platinum; Hafnium dioxide; Atomic layer deposition; Microcontact printing; Self-assembled monolayer

1. Introduction

Atomic layer deposition (ALD) is a powerful thin film growth technique that employs a sequence of self-limiting surface reaction steps to afford sub-nanometer control of the growth process [1–5]. The self-limiting adsorption reactions ensure the precise control of film thickness, conformality, and uniformity over large area. Typically, the process permits nanoscale control in the vertical direction. To extend the method to three dimensional control of materials, we have been investigating area-selective ALD techniques which will enable micro- and ultimately nano-scale definition of the lateral structure for 3D patterning. Area-selective ALD differs from conventional, subtractive lithographic patterning: it is an additive process in which material is deposited only where needed [6–13].

Our group has investigated different patterning methods for implementing the area-selective ALD process, including photolithographically-patterned SiO_2/Si substrates [7,14], direct writing by electron and photon beams [15], and soft lithography [16,17]. Here we review our recent results on area-selective ALD using soft lithography, and compare the degree of selectivity achieved for two different deposited materials. We show that good spatial control over atomic layer deposition can be achieved using microcontact-printed resists.

We have carried out area-selective ALD using soft lithography for both a metal oxide (HfO_2) and a metal (Pt). HfO_2 was chosen due to its importance in microelectronics applications. As the lateral dimensions of metal oxide-semiconductor field-effect transistors (MOSFETs) continue decreasing and higher switching speeds are required, the thickness of the SiO_2 gate dielectrics must be substantially decreased to a few atomic layers. However, the leakage current caused by direct electron tunneling from the gate to the channel increases exponentially with decreasing dielectric thickness

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[10,18]. In order to overcome this difficulty, gate dielectrics with permittivities greater than that of SiO_2, such as HfO_2, are required [19]. High-k dielectric layers allow deposition of thicker layers while retaining the same effective oxide thickness.

Pt has enormous application prospects in both catalysis and microelectronics [20,21]. For example, due to its chemical stability in both oxidative and reductive environments, and its excellent electrical properties at high temperatures [22], Pt is used as the electrode material in nonvolatile ferroelectric random access memory devices and high dielectric capacitors. It also exhibits excellent catalytic activity for a number of reactions, including the O_2 reduction reaction at the cathode of a solid oxide fuel cell (SOFC), and is especially useful at the lower operating temperatures (below 600 °C) that are desired for integratable fuel cell systems [23].

Several groups have used microcontact-printed (μCP) resists for selective ALD of films such as TiO_2, ZnO and Ru [9,11,13,24–26]. These resists have typically consisted of self-assembled monolayers (SAMs). SAMs are thin organic films which form spontaneously on solid surfaces, and are well known for modifying the physical, chemical, and electrical properties of semiconducting, insulating and metallic surfaces. Their potential applications include the control of wetting and adhesion, tribology, chemical sensing, ultra-fine scale lithography and protection of metals against corrosion [27–29]. In our area-selective ALD process, we used self-assembled monolayers made from octadecyltrichlorosilane (ODTS) to modify the chemical properties of the substrate surface. Due to the robust, covalent Si–O linkage between the molecules and the surface, films formed by ODTS demonstrate good chemical and thermal stability, and ODTS has been demonstrated as an efficient monolayer resist for a number of ALD processes [8,12].

The approach of using microcontact printing to achieve area-selective ALD consists of three key steps, as illustrated in Fig. 1. First, PDMS stamps are fabricated through standard lithographic methods and inked with ODTS precursors [30]. Second, the pattern encoded in the PDMS stamp is transferred via application of the SAM onto the substrate by microcontact printing. Third, HfO_2 or Pt thin films are selectively deposited by ALD onto areas of the substrate that are not deactivated by ODTS, and the ODTS resist is removed.

In this paper, we will show that patterned ODTS transferred onto the substrate by microcontact printing can reduce or prevent the atomic layer deposition of HfO_2 and Pt at the printed areas. Furthermore, we will compare the area selectivity and the subsequent resolution of the patterned HfO_2 and Pt fabricated through the soft lithography-based method. Finally, for the area-selective ALD of HfO_2, we will compare the selectivity and resolution of the soft lithography-based approach with the method based upon selective surface attachment on patterned SiO_2/Si.

2. Experimental

2.1. Chemical reagents

All chemical reagents, including octadecyltrichlorosilane (ODTS) (97%), toluene (anhydrous, 99.8%) and chloroform (99%), used to form SAMs were purchased from Aldrich (Milwaukee, WI) without further treatment. Poly(dimethylsiloxane) (PDMS) (Sylgard 184) was purchased from Dow Corning.

2.2. Substrates

All silicon sample pieces were cut from Si (100) wafers purchased from Si-Tech, Inc. (p-type with boron dopant; resistivity of 1.0–10.0 Ω cm). The wafer pieces were cleaned by sonication in chloroform, DI water rinsing, piranha etch, a second DI water rinsing, and finally blown dry with a N_2 flow. The result is a chemical oxide-coated silicon substrate. Thin film yttria-stabilized zirconia (YSZ) substrates, coated on Si (100), were provided by Friedrich Prinz's group at Stanford University. Two steps were used to clean the YSZ substrates [31]. First the substrates were rinsed ultrasonically, twice, for 5 min in ethyl alcohol in order to remove grease. After the first

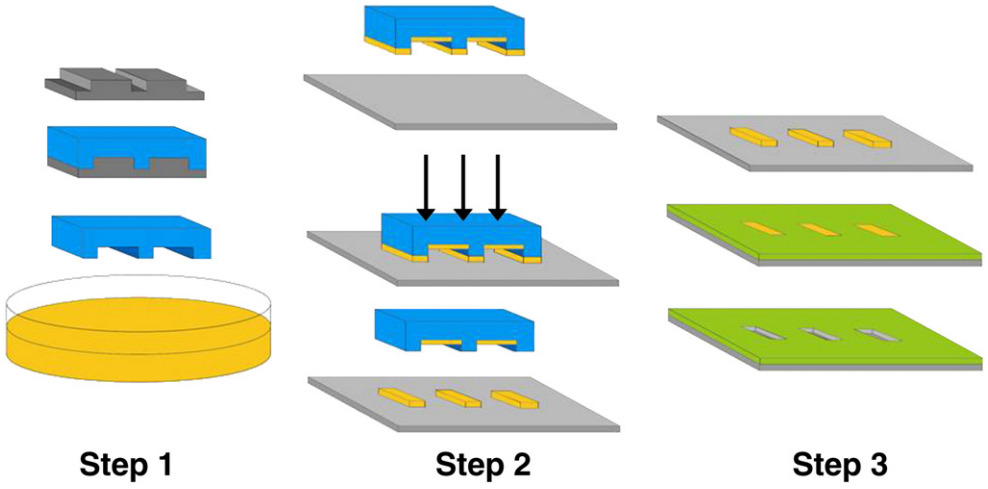

Fig. 1. Schematic outline of the procedure to fabricate patterned HfO_2 or Pt thin films using microcontact printing and selective atomic layer deposition.