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Supercritical CO_2 reactor for wafer-scale thin film deposition: reactor concept, numerical results, and Cu depositio.

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ABSTRACT

Supercritical fluid chemical deposition, frequently abbreviated SFCD, is a thin film deposition technique that employs supercritical fluids. In this deposition technique, a thin film is synthesized from a precursor dissolved in a fluid, along with a reaction reagent if necessary. This paper proposes a novel wafer-scale tool for SFCD. The reactor has a flat cylindrical interior, and the fluid is supplied at the center of the upper face. A porous plate is placed on the bottom face, at the center of which a small fluid outlet is opened. A wafer is placed directly on the porous plate without a holding device, and the diameter of the porous plate is slightly larger than that of the wafer. This reactor has a minimal interior volume and realizes radial and unidirectional flow over the entire wafer. Furthermore, the in-plane pressure distribution is completely uniform, allowing a uniform flow distribution, which was verified by computational fluid dynamics simulations. Cu films were deposited on a 100 mm silica glass wafer using $Cu(C_9H_{12}O_2)_2$ ($Cu(dibm)_2$) as a precursor. The average thicknesses were 75 nm at 185 °C and 182 nm at 200 °C,and the standard deviations were 19 nm and 14 nm, respectively. Basic film characterization was also performed.

1. Introduction

Thin films can be obtained through a chemical reaction of a precursor or mixture of precursors dissolved in a supercritical solution. This technique is called supercritical fluid chemical deposition, frequently abbreviated SFCD or SCFD. Metal deposition using this technique has been reported for Cu [1–3], Ni [2–4], Pd [2,5,6], Pt [5,7,8], Rh [5], Ru [9,10], Au [5], and Ag [11,12]. To deposit a metal, a precursor (an organometallic compound) is dissolved in $scCO_2$ along with hydrogen or another reducing agent [12] if necessary, and the metal is deposited through a thermal reaction. One example of a chemical formulation of this reaction is $ML_2 + H_2 \rightarrow M + 2HL$, where M refers to the metal and L is a ligand. The excellent capability of this technique for filling narrow features, such as nanopores [12–15], nanotrenches [2,3,16], and nanoholes [16,17], with a metal has been demonstrated successfully, which suggests that this technique may be applicable to the fabrication of small interconnects.

One promising application of metal SFCD is metallization, which is a series of processes used to embed or form interconnects in LSI or packaging components. In LSIs, the interconnect dimensions are continuously being downscaled and aspect ratios are increasing. Existing deposition techniques such as physical vapor deposition (PVD), chemical vapor deposition (CVD), and electroplating may face limitations in the fabrication of nanometer-sized interconnects. Its superior filling and conformal deposition capability make SFCD an attractive alternative.

Wafer-scale deposition is needed for microelectronic fabrication, and designing a wafer-scale deposition tool has been of interest in SFCD development. Suppression of natural convection and density uniformity are issues in designing a reactor, as supercritical fluids are dense and compressive media. Shan et al. studied a single-wafer deposition tool [18]. Their reactor basically followed the concept of conventional vacuum processors, such as metalorganic CVD (MOCVD), and used a large flow expander (nozzle or cone) to generate a uniform downflow. A large internal volume and a long residence time can lead to flow non-uniformity caused by small temperature/pressure fluctuations. A multi-wafer batch reactor was also proposed [19], in which the fluid is continuously fed through in a gap between parallel wafers. This type of batch reactor contains a number of wafers (for example: 25 wafers) and has a large reactor volume and equipment footprint. In most LSI metallization processes, different process recipes are used from

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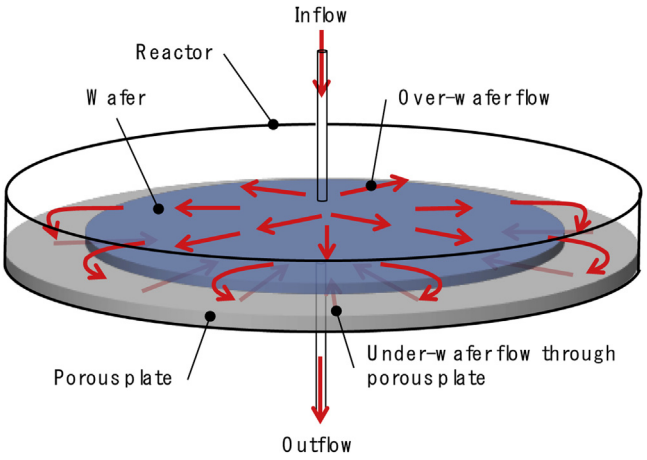

Fig. 1. Reactor schematic. The reactor has a flat disk shape. The fluid is supplied at the center of the top face, go through a porous plate and is discharged at the small outlet opened at the center of the backside plate. The arrows indicate the conceptual flow motion.

wafer to wafer. Single-wafer equipment is definitely required, and in fact no batch reactors are commercially available. In addition to single-wafer design being the focus of reference 19 rather than batch design, flow uniformity issues were not discussed and no wafer-scale experimental data were provided. In this work, we propose a new concept of a single-wafer supercritical fluid processor. Advantageous features of the reactor concept were investigated by numerical simulations. An actual deposition tool was built, and the thickness uniformity was experimentally evaluated. Basic film characterization was also performed.

2. Reactor concept and numerical results

2.1. Reactor concept

Fig. 1 shows a reactor schematic. The interior space of the reactor has a flat disk shape, like a wafer-case. The fluid is supplied at the center of the top face of the "disk". A porous plate is placed on the bottom face, in the center of which a small fluid outlet is opened. A wafer is placed directly on the porous plate, face up, and the diameter of the wafer is the same as or slightly smaller than that of the porous plate.

The incoming fluid spreads axial-symmetrically from the center to the edge of the wafer. Then, the fluid flows through the porous medium towards the outlet on the backside center. The fluid pressure drops significantly within the porous plate due to its fluid resistance, and as a result, the pressure of the reactor interior becomes very uniform, according to Pascal's law. This arrangement realizes a uniform flow distribution over the wafer.

The small reactor design allows a reduction of the time required for fluid charge and discharge, which is extremely important to reducing process time. The wafer is simply placed on the porous plate without a mechanical clamp, so the film is deposited over the entire wafer surface with maximal deposition area. The fluid in the reactor interior presses on and stabilizes the wafer, which is another reason that mechanical clamps are unnecessary. All of the above factors are crucial in designing a productive single-wafer processor.

2.2. Computational fluid simulation

Computational fluid dynamic simulations were carried out using a general finite-volume analysis software system ANSYS CFX^{TM}. A half-transverse cut reactor model was used to reduce

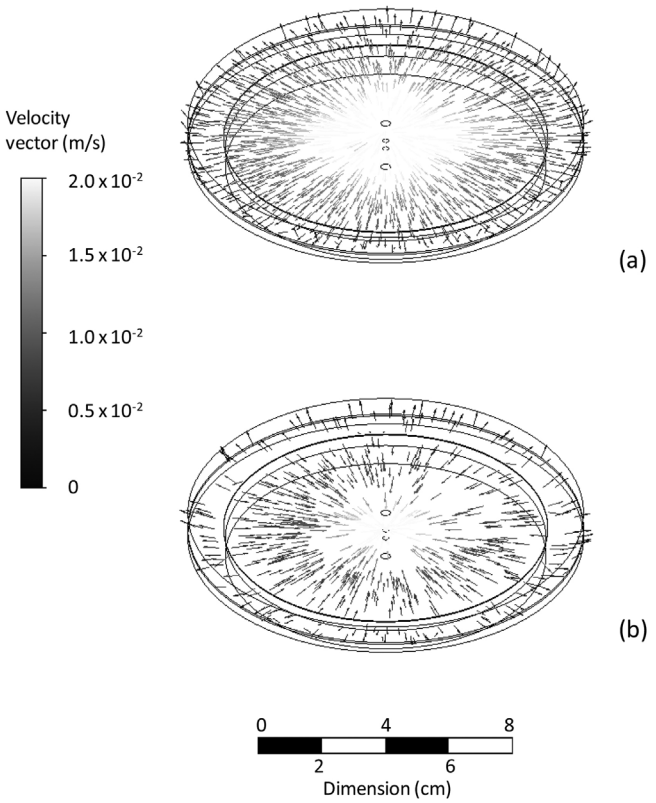

Fig. 2. Flow vector field plots within the transverse plane of the reactor interior (a) and within the porous medium (b).

calculation costs. Straight pipes were connected to the inlet and outlet of the "disk" reactor (not shown). The details of the calculation and fluid physicochemical properties are described elsewhere [20]. Porous medium volume elements were used to set a permeability of 1.11×10^{-10}, which was estimated from the Kozeny–Carman equation [21]. The wall temperature was fixed at 200 °C or 240 °C, and the temperature of the incoming fluid was 150 °C, the same as in the deposition experiments discussed afterwards.

Fig. 2(a) shows a flow vector field plot within the transverse plane of the reactor. The temperature was 240 °C, and the conversion flowrate of the supplied CO_2 was 10 mL/min at −7 °C and 10 MPa, the same as our experimental conditions (shown later). Flow is supplied at the center, where the flowrate is high (gray arrows). The incoming flow travels from the inlet towards the outer edge of the wafer where the porous media is exposed. The flowrate decreases (dark arrows) because the flow expands radially as it travels.

Similarly, Fig. 2(b) shows a transverse flow field within the porous medium. Coming in from the outermost edge, the fluid travels towards the outlet at the center. The flow field is almost the same as that shown in Fig. 2(a) (the gray scale bar is also the same), except that the flow direction is reversed. This is very obvious from the symmetric design of the reactor, as well as from the conservation of the fluid mass flow.

Fig. 3 shows radial distributions of the pressure in the reactor space (○) and in the porous medium (□) under different fluid conditions. The distributions are similar, except for the absolute pressure level. When the fluid flow rate was doubled (5 mL/min (a) → 10 mL/min (b)), the pressure also doubled. When the temperature was increased from 200 °C to 240 °C (c), the pressure increased by approximately 15% due to the resulting increase in viscosity [22]. The pressure distribution was very uniform within