Thin Solid Films xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Feasibility study into the deposition of an organic planarization layer using sequential polymerization initiated chemical vapor deposition

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ARTICLE INFO

Article history:
Received 1 October 2016
Received in revised form 31 December 2016
Accepted 9 January 2017
Available online xxxx

Keywords:
Planarization
Initiated chemical vapor deposition
Sequential polymerization
Scanning electron microscopy

ABSTRACT

In this work, we investigated the film growth and planarization properties of sequential polymerization initiated chemical vapor deposition method (SP-iCVD). Supersaturated concentration of monomer and small amount of initiator were introduced sequentially into chamber. The obtained film properties such as uniformity, polymer molecular weight and thermal stability were same or better than iCVD processed film. Additionally, good planarization of high aspect ratio (7:1) patterned wafer was demonstrated in SP-iCVD. The overburden from top of feature was within 20 nm and film thickness between isolated and dense feature areas was very uniform in this single-step process.

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1. Introduction

For decades, fabrication flows for microelectromechanical system and integrated circuit architectures have incorporated smaller and smaller feature sizes. This places a constraint on the surface flatness requirement for obtaining these critical dimensions. As such, filling and/or planarization processes are considered as one of the critical steps for device fabrication [1–3]. Processes must not damage the features and specific film properties are required for each application. For example, easy removability is necessary for pattern formation and high thermal and chemical resistance is expected for structural layer. Currently, planarization layers are obtained by a multi-step process that includes spin-coating and etch-back in order to fill isolated as well dense patterns uniformly. Spin coating is a damage-less process, but not suitable for multilayer film coatings, being a solvent based process. Consequently, a single step planarization technique that deposits a uniform film between isolated and dense features without any surface damage can improve the process efficiency.

Initiated Chemical Vapor Deposition (iCVD) is a single-step and low-energy vapor deposition process that has demonstrated polymeric thin films deposition [4–6]. In iCVD, monomer and initiator are introduced into the chamber while the pyrolysis, via a heat source, of the labile initiator produces the radicals necessary to initiate, propagate and terminate the polymerization of the monomer as it adsorbs on the cooled substrate. iCVD can be considered a polymerization without using of plasma excitation, thus it prevents plasma charging damage of the substrate. Moreover, functional films such as multi/graded layer and *co*-polymer are available because iCVD is an all-dry polymerization process [7]. iCVD polymer growth is mainly controlled by the local concentrations of reactants, the ratio between the monomer partial pressure and the saturation pressure (P_m/P_{sat}) and Monomer to Initiator ratio. Especially, surface reaction probability on planar or structural surface is strongly affected by P_m/P_{sat}. Highly conformal growth in high aspect ratio (AR) feature has been demonstrated under low P_m/P_{sat} conditions while high P_m/P_{sat} condition presents high deposition rate of polymer [8,9]. Consequently, iCVD is the promising technique for device fabrication such as through silicon via insulation and photoresist. However, the planarization process has not been reported because of iCVD conformal growth properties. A.M. Coclite et al. obtained planarized process for barrier layer with initiated plasma enhanced chemical vapor deposition method but a film thickness of twice the height of the structures was required for global planarization [10]. In this work, a feasibility study into using iCVD in an alternative deposition mode using neo-Pentyl Methacrylate (nPMA) was investigated.

2. Experimental details

The Poly nPMA (PnPMA) films were deposited onto blanket silicon wafer substrates and patterned substrates with *tert*-butyl peroxide (TBPO) as initiator in a vertical flow reactor. The liquid monomer was vaporized using Ar as a carrier gas and fed into reactor, while the initiator vapor was drawn directly from the liquid container, maintained at room temperature. Reactor walls and lid were heated to 75–80 °C to avoid monomer adsorption and polymer film deposition. During the process, the filament array located above the surface of the wafer was

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http://dx.doi.org/10.1016/j.tsf.2017.01.012
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Please cite this article as: K. Ichiki, et al., Feasibility study into the deposition of an organic planarization layer using sequential polymerization initiated chemical vapor deposition, Thin Solid Films (2017), http://dx.doi.org/10.1016/j.tsf.2017.01.012

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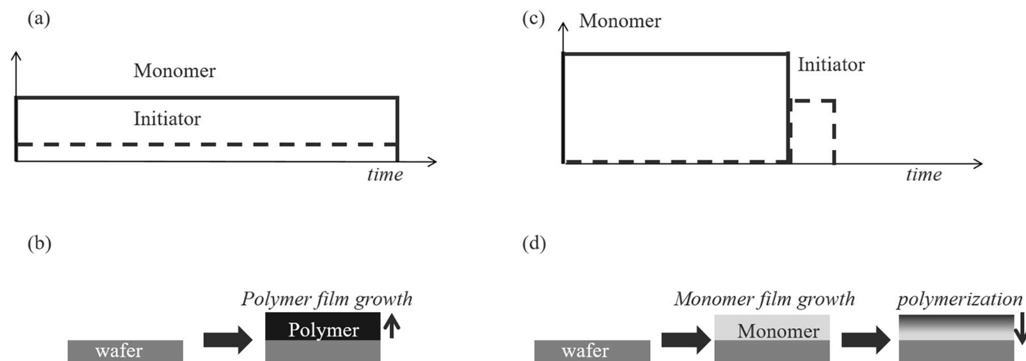

Fig. 1. (a) Monomer and Initiator flow sequence in iCVD process. (b) Polymer film growth image in iCVD process. (c) Monomer and Initiator flow sequence in SP-iCVD process. (d) Polymer film growth image in SP-iCVD process.

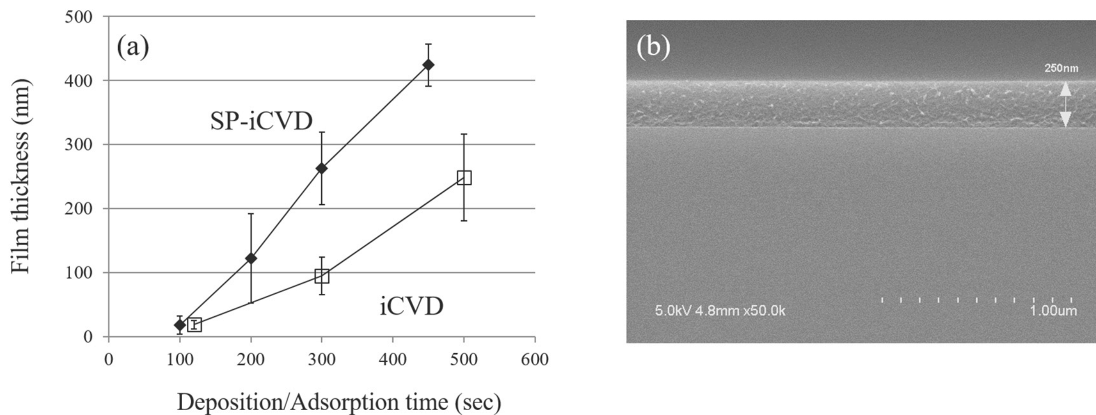

Fig. 2. (a) Comparison of SP-iCVD and iCVD PnPMA film growth on Si substrate. (b) SEM image of 250 nm SP-iCVD PnPMA film.

heated to 260 °C. Free radicals are formed by the pyrolysis of the labile initiator molecules as they flow through the filament array. Wafer surface temperature was controlled by external chiller coupled to an electrostatic chuck. nPMA and TBPO were used without further purification.

In both iCVD and Sequential Polymerization iCVD (SP-iCVD), the reactor pressure was kept constant at 266 Pa during process. Initially, filament was turned on, and Ar was injected into reactor. After reaching desired filament temperature and reactor pressure, the chemicals were then introduced into the reactor. Monomer and initiator flow were 25 and 4 sccm, respectively.

In iCVD, both monomer and initiator are introduced simultaneously during deposition sequence (Fig. 1a). The monomer vinyl bonds are activated by the radicals and polymerization is initiated on the wafer surface. Polymer propagation proceeds on the surface until stopping new monomer introduction or the other initiator radicals terminate to the activated species (Fig. 1b). Film growth is very conformal, and uniform smooth film is usually obtained in iCVD process. Process P_m/P_{sat} is usually lower than 1 to avoid monomer accumulation on wafer surface [11]. In iCVD process, the deposition process was stopped by switching off the initiator and monomer flow rate.

In SP-iCVD, the monomer and initiator are introduced sequentially (Fig. 1c). First, a monomer film is adsorbed onto the wafer surface under a supersaturated condition ($P_m/P_{sat} > 1$) followed by introduction of the initiator into the reactor once the desired adsorbed layer

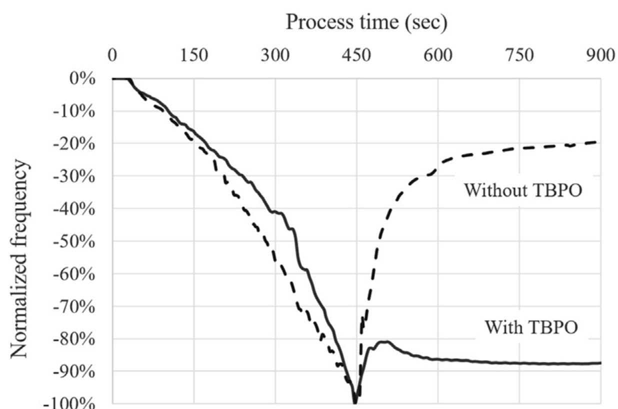

Fig. 3. Normalized QCM spectra of adsorption and desorption with TBPO (solid line) and without TBPO (dotted line) in SP-iCVD process. Adsorption time was 450 s.

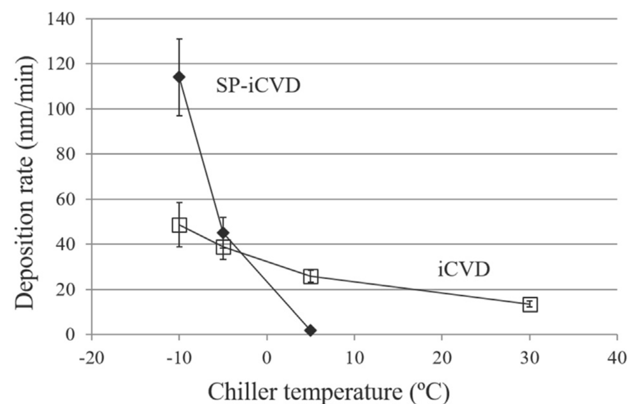

Fig. 4. Deposition rates as a function of chiller temperature for PnPMA deposition in iCVD and SP-iCVD.

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