

The Role of Supercritical CO₂ in the Drying of Porous Silicon

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Abstract – *The study of light emission from porous silicon has attracted great interest since the first observation of its photoluminescence at room temperature [1]. Recently, particular interest is devoted to supercritical fluid CO₂ [2] applications on the drying of this semiconductor. This fluid is inotoxic, non-flammable, unreactive under most conditions, leaves no liquid waste. It has a potential to ameliorate environmental safety and health impact and it enables innovative processing technologies and material protection [3]. This talk reviews the mechanism of supercritical drying of porous silicon and the role of this fluid in this process.*

Résumé – *L'étude de l'émission de la lumière du silicium poreux a attiré un grand intérêt depuis la première observation de la photoluminescence à la température ambiante [1]. Récemment, l'intérêt particulier est consacré aux applications du fluide supercritique CO₂ [2] sur le séchage de ce semi-conducteur. Ce fluide est non toxique, inflammable. Il offre des possibilités intéressantes d'améliorer la sûreté environnementale et est utilisé dans des nouvelles technologies afin d'assurer la protection matérielle [3]. Ce papier concerne le mécanisme du séchage supercritique du silicium poreux et le rôle du fluide supercritique CO₂ dans ce processus.*

Key-Words: Porous silicon – Supercritical drying – Supercritical fluid CO₂.

1. INTRODUCTION

Recent years have witnessed extensive research on porous silicon (PS) due to photoluminescence observed by Canham in 1990[1]. PS has been known for scientists since 1950s. It is a very promising material for optoelectronic devices and sensor applications[4]. It is known to form during electrochemical dissolution of silicon in HF based solution [5]. Depending on the substrate and the preparation condition during the etching, porous layers can be classified into two main types: “sponge-like” and “columnar.” In the case of sponge-like morphology small pores are randomly distributed in the film, where the cavities are surrounded by crystalline silicon wall and are all connected to the surface[6]. The columnar type PS forms on heavily doped p+ silicon and it contains long pores of typically 15 nm diameter surrounded by 5-10 nm thick silicon walls which run parallel to the <100> direction of the silicon lattice. The thickness of the porous layers is typically in the microns range. The porous layers are characterized by the porosity, i.e., the relative volume fraction occupied by the pores. Also, Porous silicon has certain properties that make it very attractive for solar cell applications. It has been proven to be a good antireflection (AR) coating for Si solar cells [7]. Pattern collapse (deformation or bending) of structures, a phenomenon related to the surface tension of rinse solution and a function of spacing and aspect ratio of patterns, becomes an increasingly serious problem as smaller features are desired. Excellent success using supercritical drying to prevent collapse by eliminating surface tension by means of supercritical fluid has been demonstrated on MEMS [2] and silicon structures, and commercial systems are available. In this paper, we present supercritical drying of porous silicon. After the presentation of advantages of supercritical fluid CO₂, We describe the role of this fluid in this process.

2. THE SUPERCRITICAL STATE

Due to gas-like transport properties and near liquid densities, supercritical CO₂-based systems offer excellent media for processing porous low-k dielectrics. Although carbon dioxide is a non-polar molecule, its solvating capability in the supercritical can be controlled by varying pressure, temperature, and co-solvents. Density of supercritical CO₂ can be tailored by changes in temperature and pressure (Figure 1)[3]. At low temperatures relatively small changes in pressure result in significant changes in density. In addition, supercritical CO₂ is non-toxic and has a relatively low critical temperature and pressure. High diffusivities and near liquid densities, coupled with no surface tension permit rapid penetration and reaction with porous low-k films[8].

For the supercritical state : Compounds heated and pressurized above their critical pressure and temperature, at which point liquid and vapor states become indistinguishable, are identified as being a fourth, supercritical fluid state with properties intermediate between liquid or gas. (Table 1) High supercritical densities (comparable to organic solvents) are sufficient to provide good solvent capability, but low enough for high diffusivity. Carbon

dioxide’s easily accessible critical point and non-hazardous nature render it the most widely used supercritical compound.

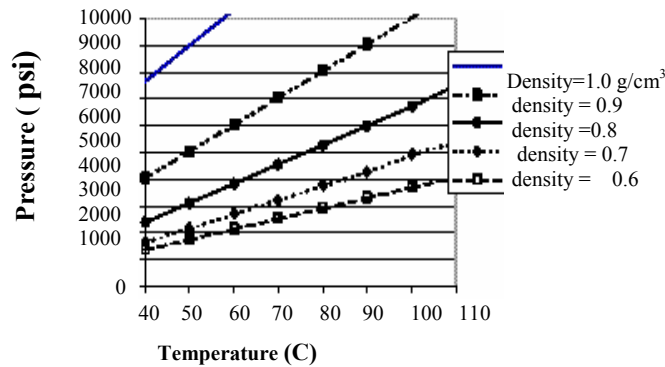


Fig. 1: The effect of temperature and pressure on the density of supercritical carbon dioxide

The high compressibility of near-critical CO₂ and the dependence of solubility, transport and other properties on density allow solvent quality to be widely varied by simple pressure control without introducing a phase interface.

Table 1: Physical properties of gas, liquid, and supercritical fluid

| | Density (g/ml) | Diffusivity (cm ² / s) | Dynamic viscosity (g / cm s) |
|---------------------|---------------------|-----------------------------------|------------------------------|
| Gas | 1x 10 ⁻³ | 1x 10 ⁻⁴ | 1x 10 ⁻⁴ |
| Liquid | 1.0 | 5x 10 ⁻⁶ | 1x 10 ⁻² |
| Supercritical fluid | 3x10 ⁻¹ | 1x 10 ⁻³ | 1x 10 ⁻⁴ |

Temperature must simultaneously be optimized for solvating power since the volatility of the solute increases with increased temperature (Fig. 2). The low surface tension of the SCF phase, another distinct advantage for manufacturing sub-micron features, allows complete wetting of complex substrates with intricate geometries. These attractive capabilities of supercritical CO (absence of surface tension, excellent mass-transfer phenomena, and controllable solvent quality) have been the impetus for many recent innovations [2].

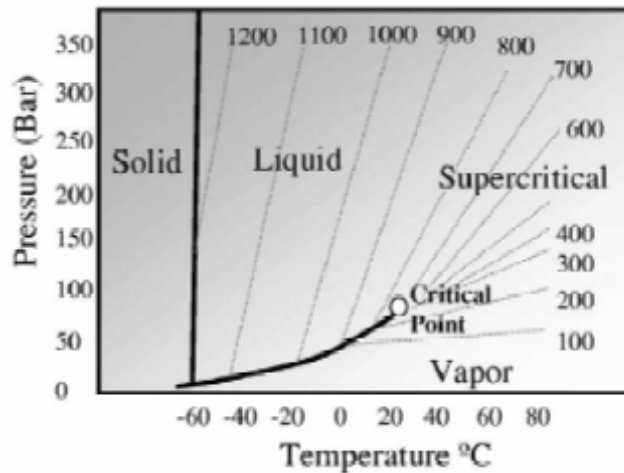


Fig. 2: P–T phase diagram with constant density lines (g/ml). An SCF (above the critical point 31.1 8C and 73.8 bar), has physical properties somewhere between those of a liquid and a gas, and a small change in pressure can induce a large change in density without phase transition [2].

3. DRYING

Pattern collapse (deformation or bending) of structures, a phenomenon related to the surface tension of rinse solution and a function of spacing and aspect ratio of patterns, becomes an increasingly serious problem as smaller features are desired (Figure 3). Excellent success using supercritical drying to prevent collapse by eliminating surface tension by means of supercritical fluid has been demonstrated on MEMS [2] and silicon structures, and commercial systems are available.. By performing an exchange step to replace resist rinse liquid with liquid CO₂ then pressurizing to supercritical and gradually reducing density until vapor is present, the rinse

liquid can be “dried” without allowing the presence of a liquid /vapor interface. Ethanol rinse liquid can be directly replaced with supercritical CO₂, whereas water rinse liquid must be replaced by surfactant-containing CO₂ or by surfactant- containing hexane prior to CO₂ exchange [2]. Resist patterns with aspect ratios of at least 7.5 (20 nm 2 wide) have been produced using these drying techniques in a resist drying apparatus designed by NTT Laboratories.

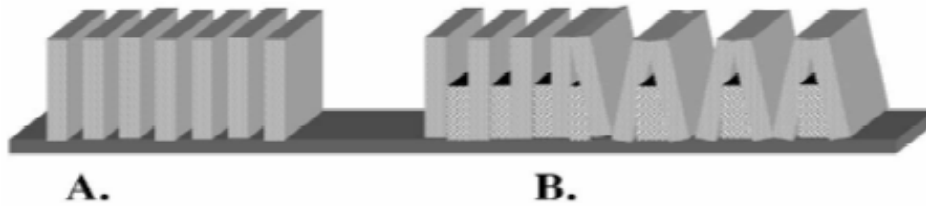


Fig. 3: (A) Desired free-standing features. (B) Collapse of features is caused by capillary forces and is a function of aspect ratio (height /width), spacing between features, and liquid surface tension.

Thus, one common characteristic of as-prepared porous silicon is its tendency to deform and crack during drying. While this is generally undesirable in terms of the mechanical stability and device type applications, the particular morphologies that are produced during solvent evaporation provide an insight into the geometry of the pore structure and PS network of the in situ sample[9]. Figure 4 presents Sequential 350x570 μm wide-field luminescence images of a 12 mA/10 min PS sample during drying.

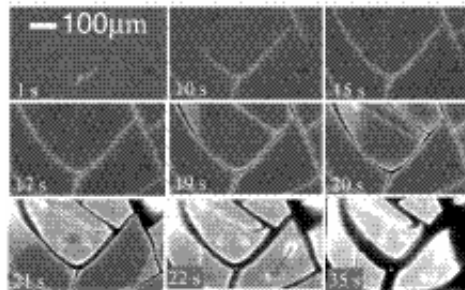


Fig. 4: Sequential 350x570 μm wide-field luminescence images of a 12 mA/10 min PS sample during drying

It is expected that the high capillary forces present during drying contribute to destroy most of the smaller nanostructures, which are probably responsible for the high photoluminescence [10, 11].

$$\Delta P = 2\gamma_{LV}/r \quad (1)$$

The Laplace formula (1) (where ΔP is the difference of pressure between liquid and vapour phase, γ_{LV} is the liquid vapour tension of the fluid, and r is the capillary radius) shows that the maximum pressure value increases when decreasing the pore diameter. The supercritical drying technique has been proposed in the recent past to avoid the destructive effects of air drying.

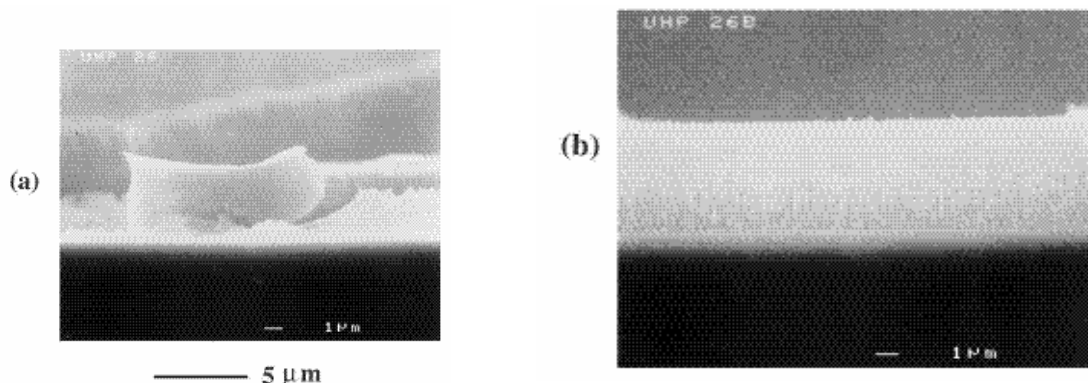


Fig. 5: Scanning electron microscopy observation of a 5μm thick p⁺ type porous silicon layer (porosity of 95%) a: dried in ambient air, b: dried with supercritical CO₂

3.1. Supercritical Drying

This technique was first used by Kistler in the 1930s and has been very useful for the processing of highly porous aerogels. Indeed the liquid has to be compressed and heated in an autoclave beyond its critical point and then converted to a gas through pressure reduction at constant temperature. The fluid used is often CO₂, for which the critical pressure and temperature are respectively 7.36 MPa and 304.1 K.

Supercritical drying is based on the exploitation of the fact that when the pressure is raised the interface between the liquid and the gas phase becomes unstable and when the pressure is larger than the critical pressure the interface gas/liquid disappears and a mixture of the two phases appears (supercritical fluid). This is the most efficient drying method. In such a technique, the HF solution is replaced by a suitable “liquid”, usually carbon dioxide, under high pressure. The phase is then moved above the critical point (31°C) by raising the pressure and temperature, as schematically shown in Figure 6 path a-b, b-c. Then the gas is removed by the supercritical liquid (Figure 6, path a-b, c-d). This drying procedure allows to produce layers with very high thickness and porosity values (up to 95 %) improving the optical flatness and the homogeneity as well. However supercritical drying is expensive and complicate to implement so other drying methods are normally employed[5].

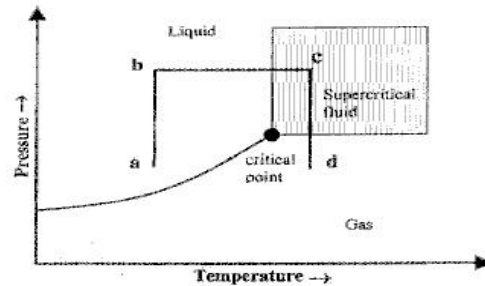


Fig. 6: Schematic phase diagram showing pressure-temperature paths used in supercritical drying

Due to eliminating the enormous capillary forces generated at liquid-vapor interface, the supercritical drying (SD) samples can keep integrity of the structure without any collapse. This technique is the most efficient method to fabricate PS and free-standing PS films with high porosity. On the other hand, the samples dried by Normal Drying (ND) method would induce collapse of the skeletons caused by these capillary forces and the probability of the collapse increases with decreasing the sizes of the nanocrystalline Si in PS. As a result, the structure and properties of the PS samples by supercritical drying is very different from those of the samples by Normal Drying[12].

4. CONCLUSION

PS exhibits unique properties due to its nanoscale structure and very active surface with enormously large area. In order to reduce the capillary stresses, many methods have been developed. Among of them the supercritical drying. In this paper, we have described the role of CO_2 supercritical fluid in the drying of this material. This drying procedure allows to produce layers with high thickness. This drying procedure allows to produce layers with very high thickness and porosity values (up to 95 %) improving the optical flatness and the homogeneity as well. the SD process can avoid the liquid-vapor phase boundary and thereby eliminate the structural collapse caused by capillary forces. This technique has been the most efficient method for fabricating PS and free-standing PS films with high porosity. SEM and Raman results show that there are obvious differences in microstructure between the SD and ND samples. Further more, the PL and optical absorption properties of the PS dried by SD are also different from those of the sample by ND. However supercritical drying is expensive and complicate to implement so other drying methods are normally employed.

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