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Deposition and electrostatic removal of gaseous organic contaminants on substrate surfaces

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ABSTRACT

The adhesion behavior of di-n-butyl phthalate (DBP) onto different substrates (quartz, glass, and silicon) used as wafer surfaces was studied by using an in situ UV spectrophotometric technique. The results from the closed cell experiments revealed that greatest extent of DBP adhesion occurred on the quartz chip ($0.154\,\mu g\,cm^{-2}$), followed in the order by the glass ($0.054\,\mu g\,cm^{-2}$) and silicon ($0.039\,\mu g\,cm^{-2}$). By means of the in situ spectrophotometric observation, application of an electrical field at $290\,V\,cm^{-1}$ in the cell proved to be effective in inducing charging of DBP aerosols, which were consequently attracted towards the electrodes. This method can be applied to wafer storage and transport equipments to prevent wafer contamination from material outgassing representative by DBP.

1. Introduction

The design of most modern electronics and communication industry tools allows for intratool storage and transport under stringent cleanliness control by purging with high-purity nitrogen gas. In such systems, the level of oxygen and water vapor is on the order of a few parts-per-million (ppm) or less. Although this approach provides a very clean ambient environment from a macroscopic (i.e., particulates) standpoint, it can lead to increased levels of microscopic (i.e., molecules) contamination that must be eliminated by special measures.

The type of microcontamination is known as the airborne molecular contamination (AMC), a rather generic term because the contaminants may be in the form of a gas, vapor, or even an aerosol, each with vastly different chemical natures [1]. Even though the control of these AMCs has been recognized as an essential design requirement for all state-of-the-art semiconductor manufacturing facilities, the complexity of the problem, which includes the variation in the source and ambient concentrations as well as the impacts on the fabrication process, largely hampers the development of an effective or standardized control strategy.

The purpose of this study is two folds: (i) to develop a convenient and cost-effective sampling and analytical procedure tailored to make frequent quantitative measurements of organic AMCs that exist in a clean room ambient and deposit on wafer surfaces and (ii) to investigate the feasibility to remove the contaminant from conductive surfaces via electrostatic force, which is induced by a close-spaced copper electrodes at a high voltage difference. In this study, di-n-butyl phthalate (DBP, CAS# 84-74-2), a representative compound belonging to a family of plasticizer compounds that exist ubiquitously, are selected as the calibrating organic AMC. These phthalate esters, including DBP, have been targeted as one of the most detrimental organic AMC in microelectronics device fabrication processes, as they are difficult to remove from wafer surfaces once deposited [2,3]. The procedures described in this report include an analytical technique using ultraviolet (UV) spectrophotometry capable of quantifying contaminants at low parts-per-billion (ppb) levels. Furthermore, a simple but innovative method of applying electrostatic force between the copper surface and the phthalate anions to prevent the adsorption of phthalate anion onto the wafer surfaces is demonstrated here.

2. Materials and methods

2.1. Optical absorbance measurements and substrate adhesion study

Analytical-grade DBP obtained from Acros Organics (USA) was used for the preparation of liquid standards by dissolving DBP in n-hexane (analytical-grade, Sigma–Aldrich, USA), a solvent exhibiting the least interference to DBP during UV spectrometric analysis. The stock solution with DBP concentration at 1000 ppm (by volume),

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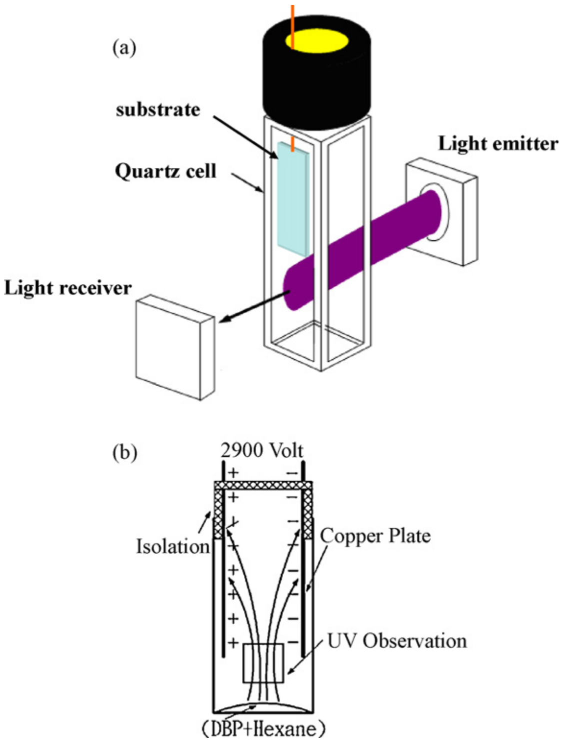

Fig. 1. Schematics of the experimental apparatus: (a) UV spectroscopy for DBP detection in a quartz cell and (b) electrical field induced by a pair of copper electrodes inside the quartz cell.

corresponding to 1047 μg cm^{-3}, was prepared for the ensuing experiments.

As shown in Fig. 1a, a Helios Alpha (Thermo Scientific, USA) spectrophotometer transmits light through a quartz rectangular cell having a path length of 10 mm. To validate the in situ concentration measurement technique, an aliquot (10 μl) of the DBP solution having been serially diluted (0.05–500 ppmv) from the stock solution was injected to the bottom of the sealed cell. The aliquot was allowed 10 min to evaporate, and then was subjected to UV spectrophotometer analysis.

For the substrate adhesion study, a rectangular slide of various types of substrate (quartz, glass, silicon) with the same dimensions (length: 20 mm; width: 8 mm) was suspended by a thin metal wire in the upper portion of the cell. The substrate pieces to be tested were cleaned with acetone, followed by mild oven drying at 60 °C before use. After adding 10 μl DBP (52.3 μg cm^{-3} as a solution in hexane) into the cell and allowing 10 min to evaporate, the sample slide was withdrawn and flushed with hexane (2 ml) to dissolve the surface-bound DBP, and then underwent ex-situ UV spectrophotometric analysis for quantification. Calibration curves covering DBP concentrations (0.02–5.0 μg cm^{-3} in hexane) were established separately. Since the cell material is also made of quartz, an experiment without the placement of a substrate was also performed to serve as the blank control.

2.2. *Electrostatic force to remove DBP*

As shown in Fig. 1b, two copper electrodes were fixed along the internal wall of the quartz cell, and a potential of 2.9 kV was applied to induce a charging field of 290 V cm^{-1}. After introducing an aliquot of a diluted DBP solution to the bottom of the cell and allowing DBP to equilibrate, the charge field was activated, and the evolution of the DBP concentration in cell ambient was recorded in situ by the UV spectrophotometric technique.

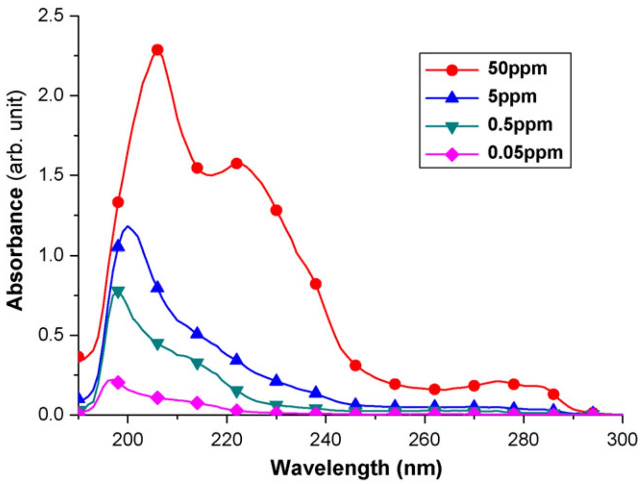

Fig. 2. UV–vis absorption spectra of DBP in n-hexane solution at various DBP concentrations.

3. Results and discussion

3.1. *Optical absorbance measurements*

Fig. 2 shows the UV absorption spectra of the DBP in n-hexane solution at different mass concentrations introduced to the cell. It should be noted that these spectra have been adjusted to eliminate the absorbance interference from n-hexane. DBP exhibits broad absorption peaks that shift towards shorter wavelength at dilute concentrations, centering at 228 nm for the concentration of 523 μg cm^{-3}, 208 nm (52.3 μg cm^{-3}), 202 nm (5.23 μg cm^{-3}), 200 nm (0.523 μg cm^{-3}), and 198 nm (0.0523 μg cm^{-3}). None of the spectra shows any absorbance at visible range, though those corresponding to 52.3 μg cm^{-3} and 523 μg cm^{-3} exhibit a shoulder at 216 and 265 nm, respectively.

The spectrophotometric calibration gave a linear range up to 5.23 μg cm^{-3}, beyond which the Beer–Lambert Law appeared to be violated. Given that the vapor pressure of DBP is approximately $4 \pm 2(\times 10^{-5})$ mmHg at 25 °C [4], the DBP saturation vapor concentration is in the range of approximately 0.03–0.10 ppmv under close-cell condition. Over-saturation leads to condensation that eventually interferes with the light absorbance. In this study, condensates became visible when injected concentration was over 0.5 ppmv, however the linear spectrophotometric curve holds for concentration up to 5.23 μg cm^{-3}.

3.2. *DBP adhesion tendency on different surfaces*

Fig. 3 shows the absorption spectra of the DBP flushed from the three types of substrates after 10 min of adhesion in the cell. Again, each absorption spectrum has been individually adjusted to discount the absorbance by n-hexane as the solvent. Evidently, the greatest tendency of DBP adhesion occurred for the quartz substrate, with an adhesion mass of 0.247 μg (corresponding to a surface density of 0.154 μg cm^{-2}), followed in the order by the glass (0.054 μg cm^{-2}) and the silicon substrate (0.039 μg cm^{-2}). Blank control experiment resulted in a greater degree of DBP surface density on the cell wall than that of the quartz substrate, possibly due to the spatial variation of DBP adhesion because the location of the UV beam in the spectrophotometer emitting through the cell was confined to a very small window. While a number of studies have focused on the deposition of phthalate esters and other organic contaminants on silicon wafers [1–3,5,6], those that directly compare the extent of contamination on different substrate surface are meager. It is conceivable that the DBP molecule, composed of highly