



Wafer-level detection of organic contamination by ZnO-rGO hybrid-assisted laser desorption/ionization time-of-flight mass spectrometry

Kookjoo Kim^a, Kiju Um^a, Cheolsang Yoon^a, Won Sun Ryoo^b, Kangtaek Lee^{a,*}

^a Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 03722, Republic of Korea

^b Department of Chemical Engineering, Hongik University, Seoul 04066, Republic of Korea

ARTICLE INFO

Keywords:

SALDI-TOF MS
ZnO
Reduced graphene oxide
Organic contamination
Benzo[a]pyrene
Semiconductor

ABSTRACT

A technique for wafer-level detection of organic contaminations via surface-assisted laser desorption/ionization time-of-flight mass spectrometry was developed. To replace the organic matrix in matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, zinc oxide-reduced graphene oxide (ZnO-rGO) hybrid was prepared by a hydrothermal reaction and used as the matrix in the detection of benzo[a]pyrene (B[a]P). By varying the rGO content and the amount of hybrid, the optimal rGO content in the hybrid for the detection of B[a]P was determined to be 4 wt% and the optimal amount of hybrid was 20 ng. The limit of detection of this method was found to be 1.6×10^{14} C atoms cm^{-2} , which is lower than the concentration of residual organic contamination at which serious failure occurs during semiconductor fabrication. This method was also successfully used to detect other aromatic and aliphatic species on a semiconductor wafer. This approach is fast, accurate, simple, and inexpensive compared to other conventional methods, and can be used to identify localized micro-contamination in the semiconductor industry.

1. Introduction

The recent demand for miniaturization in semiconductor fabrication has led to an increase in the number of processing steps, which makes semiconductor packages (or wafers) more susceptible to micro-contamination [1,2]. Because micro-contamination has a detrimental impact on the performance of semiconductor devices and can result in yield losses up to 50%, detection of residual contaminants on semiconductor wafers is crucial for quality control [3]. In the bid to achieve a sub-10 nm node in advanced patterning technology, the use of self-aligned double and even quadruple patterning has recently surged [4]. Even though various organic materials used for the photoresist and anti-reflective coating during the patterning process are removed by repeated cleaning, residues of these materials remain on the silicon wafer even after cleaning. Therefore, identification of organic contaminants has become a critical issue in the semiconductor industry [5].

Because analysis of the semiconductor yield requires defect coordinates as well as information regarding the process steps, equipment, input materials, etc., it is necessary to identify organic contamination in localized areas of interest. However, current methods for the detection of organic contaminants involve heating the entire wafer, making it impossible to get information on residual organic contaminants localized on the wafer surface [6]. Although various

characterization techniques have been used to solve this problem, a few drawbacks still remain. For instance, electron microscopic techniques such as transmission electron microscopy (TEM) and scanning electron microscopy (SEM) with energy dispersive spectroscopy can identify the presence and types of atoms, but not the types of organic contaminants. In addition, it is difficult to apply spectroscopic techniques such as Fourier-transform infrared and Raman spectroscopy due to interference from the substrate and the multilayered structure of the semiconductor devices. In gas or liquid chromatography, collecting localized contaminants from the wafer is required in the sample preparation step, which is time-consuming and often problematic.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) with weak ionization technology is considered as a suitable technique because it can provide information on the type and location of the contaminants. In this technique, an organic matrix is used to absorb energy from a pulsed laser and transfer it to the analyte, thereby facilitating desorption and ionization. However, the use of organic matrices such as α -cyano-4-hydroxycinnamic acid and 3,5-dimethoxy-4-hydroxycinnamic acid makes the technique inappropriate for the detection of small molecules (M.W. < 1000 Da) because of matrix interference [7]. To overcome the limitations of the conventional matrix and increase the sensitivity [8], surface-assisted laser desorption/ionization time-of-flight mass

* Corresponding author.

E-mail address: ktlee@yonsei.ac.kr (K. Lee).

spectrometry (SALDI-TOF MS) has been developed by replacing the matrix with nanoparticles of graphene, semiconductor, Au, or Ag. However, these species still have drawbacks such as toxicity and high cost.

ZnO nanoparticles are non-toxic, inexpensive, and widely used in many applications, including light emitting diodes [9,10], solar cells [11], photo-catalysis [12], and sensors because of their large bandgap energy and ability to absorb UV light. Reduced graphene oxide (rGO) with a unique 2D structure has also been widely studied as an electronic material and adsorbent because of its high conductivity, high electron mobility, and large surface area [13–15]. Therefore, ZnO nanoparticle-rGO hybrids that combine the UV absorption characteristics of ZnO and the adsorption characteristics of rGO have been studied in various fields such as photo-catalysis, supercapacitors, and photodetectors [16,17]. Herein, we prepare a ZnO-rGO hybrid to replace the existing organic matrix used in MALDI-TOF MS, and develop SALDI-TOF MS techniques for analysis of organic contaminants such as polycyclic aromatic hydrocarbons (PAHs) on silicon wafers.

2. Materials and methods

2.1. Materials

Silicon wafers (< 100 >; p-doped) were purchased from WRS Materials. Zinc acetate dihydrate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, 99%), sodium nitrate (NaNO_3 , 99%), potassium permanganate (KMnO_4 , 99%), pyrene (Pyr, 98%), anthracene (Ant, 99%), and benzo[a]pyrene (B[a]P, 96%) were purchased from Aldrich. Graphite powder (99.8%), potassium hydroxide (KOH, 99.98%), and hydrogen peroxide (H_2O_2 , 29–32 wt% in H_2O) were purchased from Alfa, and octadecyltriethoxysilane (OTES) was purchased from Tokyo Chemical Industry. Methanol (99.5%), sulfuric acid (H_2SO_4 , 98%), acetone (99.8%), isopropyl alcohol (IPA, 99.7%), and hydrochloric acid (HCl, 35%) were purchased from Duksan, and hydrofluoric acid (HF, 47–51%) was purchased from Fluka. Deionized (DI) water from a Millipore water (18 M Ω cm) purification system was used for all experiments. All chemicals were used without further purification.

2.2. Preparation of ZnO-rGO hybrid

ZnO particles were synthesized by using the previously reported method [18]. Briefly, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (7.38 g) was dissolved in methanol at 60 °C. KOH (3.7 g) dissolved in methanol (16.25 mL) was added dropwise to the aforementioned solution and allowed to react for five days with magnetic stirring at 60 °C. The resulting particles were separated by centrifugation (3000 rpm, 15 min), washed with methanol and DI water, and vacuum dried at 50 °C.

Graphene oxide (GO) powder was prepared by the modified Hummer's method [19]. H_2SO_4 (37.5 mL) was slowly added to a flask containing NaNO_3 (0.38 g) and graphite powder (0.5 g) in an ice bath with magnetic stirring. After 30 min, KMnO_4 (2.25 g) was slowly added and stirring was continued at room temperature for five days. Dilute H_2SO_4 (5 wt%, 70 mL) was added to the mixture at room temperature and stirred for 2 h at 90 °C, followed by addition of H_2O_2 (3 mL) with stirring for 2 h at room temperature. Finally, the product was centrifuged at 6000 rpm for 10 min and washed with a mixture of H_2SO_4 (3 wt%), H_2O_2 (0.5 wt%), and HCl (3 wt%). The product was repeatedly washed with DI water until the pH became neutral and vacuum dried at 40 °C overnight [19].

To prepare the ZnO-rGO hybrid, ZnO particles (0.5 g) were added to a suspension of GO (GO/(ZnO + GO) = 2, 4, 8 wt%) in a mixture of DI water (65 mL) and ethanol (32.5 mL), and the mixture was placed in a Teflon-lined autoclave vessel and stirred at room temperature for 2 h. The temperature was then raised and kept at 180 °C for 12 h, during which the GO was converted to rGO to form the ZnO-rGO hybrid. The resulting precipitates with 2, 4, and 8 wt% rGO (denoted as ZR-1, ZR-2,

and ZR-3, respectively) were separated by filtration and washed by repeated cycles of centrifugation (3000 rpm, 20 min) and redispersion in DI water. To obtain the hybrid in powder form, the product was vacuum dried at 50 °C overnight [20].

2.3. Detection of PAHs using ZnO-rGO hybrid

Si wafers were cleaned by successive ultrasonication in acetone and IPA and immersed in a 0.5% HF solution for over 10 min to remove the native silicon oxide [21,22]. The Si wafer was then rinsed with DI water and vacuum dried for 30 min. Stock solutions of PAHs were prepared in acetone (1 mg mL⁻¹) and diluted with DI water to the desired concentrations (0.1–100 ng μL^{-1}) in an acetone/water mixture (60:40, v/v) [23]. The wafer surface was contaminated by placing the PAH solutions (2 μL) on Si wafers using a micropipette (Fig. S1), and vacuum dried. The surface concentration of B[a]P on the wafer (in C atoms cm⁻²) was calculated from the average contaminated area of 0.0225 cm². The ZnO-rGO hybrid in DI water (2 μL , 10 ng μL^{-1}) was dropped onto the dried spots of PAHs using a micropipette and vacuum dried for 30 min for the MALDI-TOF MS experiments.

2.4. Characterization

The size and morphology of the synthesized ZnO-rGO hybrid were characterized by transmission electron microscopy (TEM, JEM-F200, JEOL). The absorption spectra of the hybrid were obtained by UV-Vis spectroscopy (SPECORD 210 PLUS, Analytik Jena). The photoluminescence (PL) spectra of the hybrid were obtained with λ_{ex} at 355 nm using a spectrofluorometer (LS-55, Perkin-Elmer). The crystalline structures of the ZnO particles and ZnO-rGO hybrid were studied using the powder X-ray diffraction (XRD) (Rigaku, MiniFlex) with Cu K α radiation. MALDI-TOF MS (Ultraflextreme, Bruker) experiments were performed with a 355 nm Smartbeam-II Nd:YAG laser in the positive ion mode. Averaged spectra were obtained from 60 measurements with 500 laser shots per spectrum in the mass range from m/z 100–1000. The signal-to-noise values were calculated using the automatic signal-to-noise calculator in the Ultraflextreme analysis program.

3. Results and discussion

3.1. Detection scheme of organic contaminants using ZnO-rGO hybrid

The ZnO-rGO hybrid was prepared via hydrothermal reaction between ZnO nanorods and rGOs, and was explored as a prospective matrix for SALDI-TOF MS analysis. Fig. 1 shows the scheme for detection of the organic contaminants using the ZnO-rGO hybrid as a matrix. The main role of rGO in the hybrid is to adsorb the organic contaminants through π - π interaction or hydrophobic interaction [24]. The

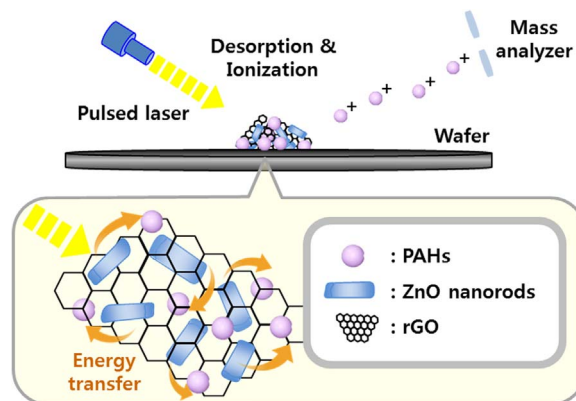


Fig. 1. Scheme for SALDI-TOF MS detection of contaminants using ZnO-rGO hybrid as a matrix.

Download English Version:

<https://daneshyari.com/en/article/7676770>

Download Persian Version:

<https://daneshyari.com/article/7676770>

[Daneshyari.com](https://daneshyari.com)