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Qualitative and quantitative characterization of outgassing from SU-8

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ABSTRACT

SU-8 is often used as a structural material in Microsystems. In this work, the outgassing characteristics from such cross-linked SU-8 layers are studied using mass spectrometry and gas-chromatography techniques. With these methods the composition of the released matter can be identified, also the outgassing rate can be quantitatively characterized. A qualitative estimate of outgassing from SU-8 is given for cross-linked layers. The effect of hard-bakes is studied in situ by measuring at typical hard-bake temperatures. These tests indicate that a hard-bake is needed to provide good performance in UHV environments. Using gas-chromatography the outgassing rate from SU-8 is determined. The total outgassing rate is inversely proportional with time which further illustrates the effect of a hard-bake step.

1. Introduction

In microtechnology SU-8 [1] is widely used for making high aspect ratio permanent structures. Many important material aspects have been investigated, as recently summarized in a review article [2]. Especially the lithographic patterning capabilities and mechanical aspects have been widely studied. Outgassing remained, to the best of our knowledge, undocumented. With some applications SU-8 structures are used in gaseous environments with a critical composition [3], other applications would have SU-8 structures operating in vacuum [4]. In these cases the impact of the SU-8 on the ambient is of vital importance. Precise characterization of and influence over outgassing from SU-8 is also important when SU-8 is used in wafer-scale packaging [5].

In this study, we present our investigations on the outgassing of SU-8 using time-resolved mass spectrometry (MS) and gas-chromatography.

2. Experimental

The SU-8 layers under study are formed on top of bare 4″ Si wafers. To prevent additional outgassing signals the wafers are first cleaned extensively in fuming HNO_3 at room temperature (10 min) and 69% HNO_3 at 95 °C (10 min) and subsequently rinsed in DI water. After this a short 2% HF dip is performed to remove native oxide, the hot 69% nitric acid step is repeated to regrow a thin chemical oxide and the substrates are rinsed again. After a 10 min dehydration bake at 120 °C the SU-8 layer is deposited by spin coating at 3000 rpm, a primer is not used. The wafers are given a 20 min Soft-Bake at 95 °C, using a hotplate, to solidify the resist layer. Next a blanket UV exposure with a dose of 290 mJ/cm^2 is performed to initiate cross-linking of the entire layer. A post-exposure bake is performed for 10 min at 80 °C. All bakes are done using long ramp-up and ramp-down times as per instructions given by the supplier [1]. The wafers are diced into 2 cm × 2 cm samples using a Disco DAD-321. Immediately after drying (using a N_2 spray gun) the samples are packaged in Al foil that is folded twice around the sample, the packaged samples are stored in sealed bags until they are measured. Some samples have received an additional 10 min hard-bake (HB) at 150 °C, also on a hotplate, prior to packaging.

All initial measurements are performed on layers of SU-8 50 of 50 μm thick. Additional measurements on thinner layers of 2 and 10 μm have also been performed. For these SU-8 formulations with a lower viscosity are used (SU-8 2 and SU-8 5, respectively), the spin speeds are lower and the bake times are shorter.

Two analysis techniques have been used. For MS analysis the SU-8 samples are placed in a vacuum chamber, a mass spectrometer (Pfeiffer QMS Prisma) is connected to monitor the gas flow coming out of the system. The specimen chamber can be elevated in temperature by resistive heating.

Further measurements are performed using a combined gas-chromatography and mass-spectrometry technique (GC–MS). The samples are heated in an oven that is flushed continuously with

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N_2. The outgassed components are adsorbed (except for the carrier gas) using a Gerstel TDSA tube and after a set period the sampled mass is released and injected into a gas-chromatography column (Agilent 5975) in which the exact chemical composition can be identified. This sampling is repeated over time to create a quantitative measure of outgassing rate and mass (accuracy is ∼5%). The technique is not sensitive for compounds with a mass lower than ∼40 a.m.u.

3. Results and discussion

Fig. 1 shows a series of mass/charge spectra obtained from a sample that has received a 150 °C hard bake. For clarity only the part with $m/q > 30$ is shown. During the scans the temperature is increased to 200 °C and then allowed to cool down to room temperature again as indicated. At increased temperature we see heavier compounds (in the range $m/q > 50$) being released (Fig. 2). During the whole cycle m/q 44 is abundantly present. Although there is also a large background signal for m/q 44 (as can be seen after cooldown to room temperature) there is an increased contribution at elevated temperatures. The main candidates for this mass signal are CO_2 or propane (as suggested in [6]). An extended GC–MS measurement is performed to capture any possible propane contribution. This involves extra strong cooling to improve the collection efficiency of such very volatile gases. However, no traces of propane have been found in any of the samples. Although CO_2 cannot be measured using CG–MS the complete absence of propane suggests that during the measurement (at 150 °C) the material is decomposing and ultimately is released in the form of CO_2.

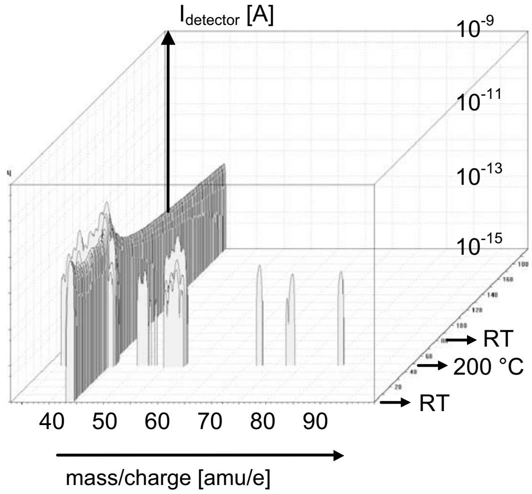

Fig. 1. Outgassing measured, using a QMS, over time from a sample of SU-8 50 heated from room temperature to 200 °C and then cooled down again (as indicated).

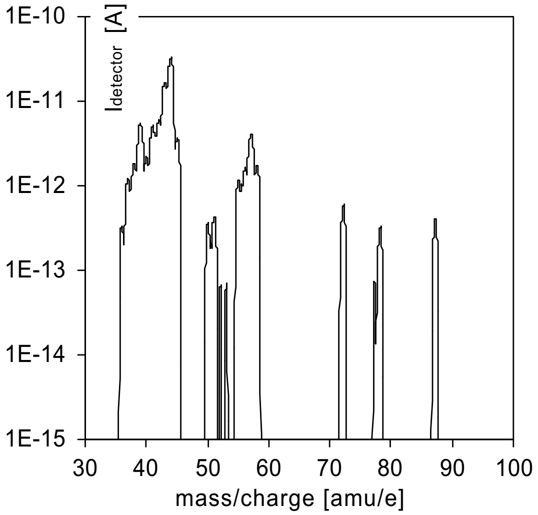

Fig. 2. Typical outgassing spectrum of the material (50 μm SU-8) at the moment when $T = 200$ °C, this is when most material is released.

The mass spectrometry measurements show significant outgassing contributions of heavier compounds (in the range $m/q = 50$–200). After heat treatment the outgassing is limited. This provides a process window for the use of SU-8 in vacuum and/or hermetically sealed packages. If a hard-bake of at least 150 °C can be allowed the outgassing levels are comparable to Kapton foils of the same area [7]. Kapton is commonly used in gas-filled detectors similar to those of the SU-8 based system in [3].

The GC–MS measurements indicate that most of the outgassing is constituted by butyrolactone (GBL, the solvent of the SU-8 resin), propylene carbonate (the solvent of the photo-acid-generator (PAG)), benzene and di-phenyl-sulfide which is a component of the PAG. Examples of GC–MS spectra are shown in Fig. 3. These show the outgassing at the start of the measurement series and at the end of the series (in this case after 80 min).

Using GC–MS we have determined the total outgassing rate in terms of weight loss over time. Fig. 4 shows the development over time of outgassing rates for various compounds as well as for the total for a sample with 50.9 μm thick SU-8. In addition samples with layers of 1.7 and 9.2 μm have been measured. The thickness values are determined by step-height measurements using a Veeco Dektak 8 profilometer in combination with cross-section SEM inspections.

To characterize the level of outgassing fits of the shape described in the formula below are made to the measured time-resolved outgassing rates, q.

$$q = q_0 \cdot t^{-\alpha}$$

Fig. 5 shows a plot of the level of outgassing rate defined as the offset constant q_0 plotted vs. the SU-8 layer thickness. The almost constant slope suggests that the outgassing can be characterized with a volume emission, in this case its value is approximately 19 $\mu g\,cm^{-3}\,min^{-1}$.

The slopes (α) of the fitted outgassing rates are in most cases close to unity.

The GC–MS measurements are performed over a fairly long period at elevated temperature under normal atmospheric pressure (under nitrogen). This means the measurement itself is very similar to a hotplate hard-bake at 150 °C. Hard-bake steps have been often discussed, some claiming they promote cracks [8] others claiming that they provide stress relief and can overcome problems with cracks and adhesion [9]. Recent findings on SU-8 adhesion properties indicate that hard-bake steps can have a strong positive effect on adhesion strength [10]. The impact of a hard-bake on the functionality of the device has to be carefully investigated, but a significant benefit in terms of outgassing characteristics is clearly present. The outgassing rate is inversely proportional to the bake time. From the given plots (Figs. 3–5) we see that at a temperature of 150 °C a hard-bake in the order of 10–30 min is very effective.

As mentioned earlier outgassing from some samples show a clear GBL contribution, in other samples, however there was little or no GBL found. This indicates that the remaining solvent concentration is not a very well controlled parameter despite strong efforts to keep processing and packaging procedures repeatable.

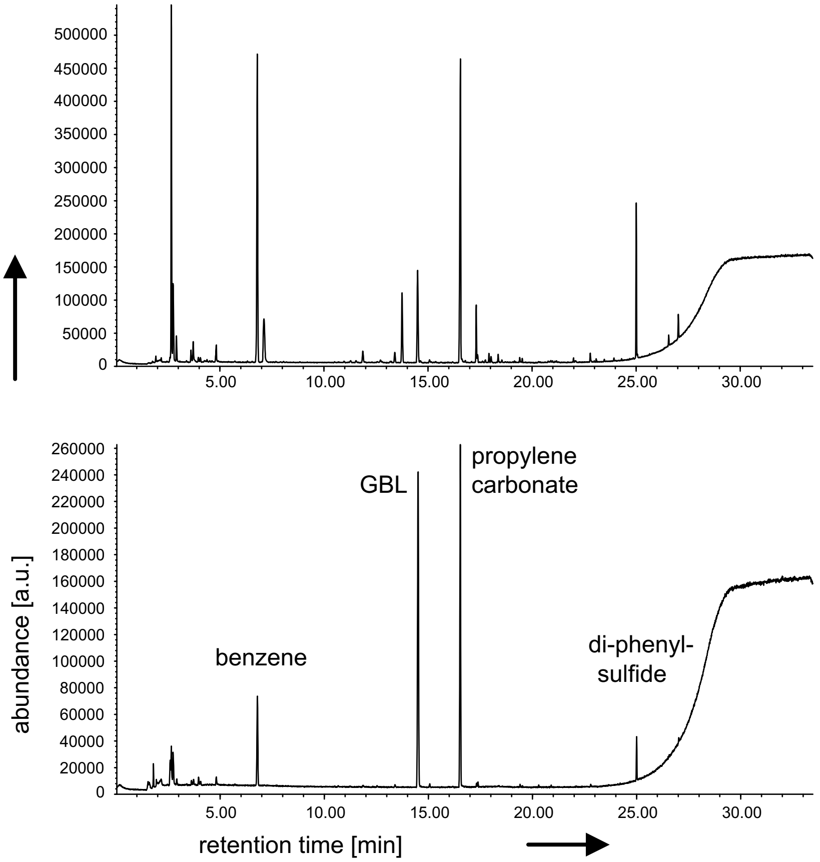

Fig. 3. GC–MS spectra at the start of the measurement (top) and after 80 min (bottom) illustrating that after a certain thermal budget (e.g. a hard-bake) outgassing is limited to only several compounds.

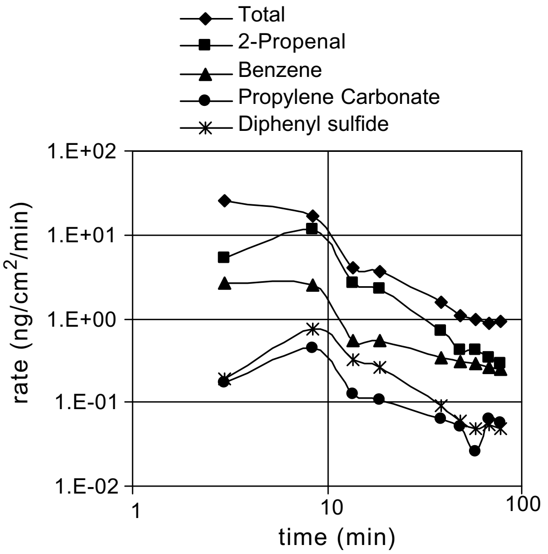

Fig. 4. Total outgassing rate as a function of time for an SU-8 50 layer of 50.9 µm thickness, measured using GC–MS. The datapoints represent the average outgassing rate over a sampling time of 5 min.

Because the layer thicknesses were all found to be as expected (in accordance with known spin-curves) the starting material must be comparable in all cases. The variation in final solvent concentration might be due to environmental conditions, similar to the results on SU-8 adhesion presented in [10].

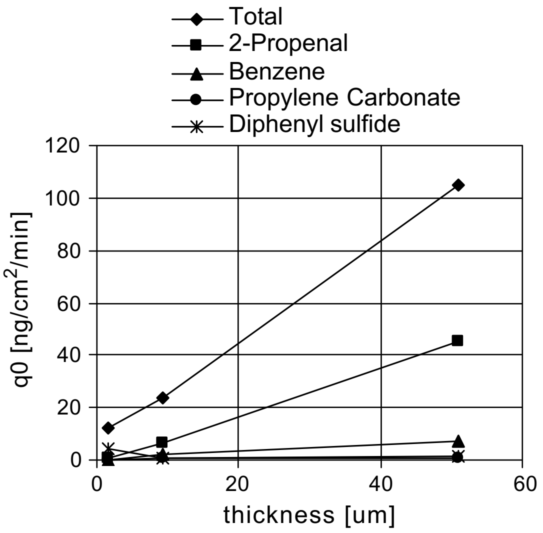

Fig. 5. Values of the linear constant q_0 (see text) for different compounds as well as for the total, plotted vs. thickness of the SU-8 layer.

The variation in outgassing rate of heavier, less volatile, compounds like di-phenyl sulfide was found to be much less variable.

4. Conclusions

Several methods are used to characterize the release of gaseous species from solid, fully processed, SU-8 layers. The qualitative (MS) and quantitative (GC–MS) measurements lead to the conclusion that a hard-bake of 150 °C is very beneficial for outgassing from SU-8 structures the outgassing rate is inversely proportional with time. The outgassing level is comparable to Kapton.

The main volatile components are benzene, 2-propenal, GBL, propylene carbonate and di-phenyl-sulfide. Further, a strong outgassing signal with mass/charge of 44 amu/e is identified. Since no measurable amount of propane is found we conclude that this signal is caused by CO_2 originating from decomposition of the material.

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