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Infrared monitoring system for the detection of organic contamination on a 300 mm Si wafer

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An infrared (IR) monitoring system has been developed for the detection and characterization of hydrocarbon contamination on 300 mm (12 in.) Si wafer surfaces. IR propagates through the Si wafer, internally reflecting about 600 times, which enables us to detect a trace of organic contamination on the wafer surface. The present system allows for the detection of hydrocarbon contamination on 300 mm Si wafer surfaces with a contamination level of below 10^{11} carbon atoms/cm^2. [S0003-6951(99)03830-9] © *1999 American Institute of Physics.*

In the fabrication of integrated circuits, preparing chemically clean silicon surfaces is quite important. One of the most widely used cleaning techniques is chemical oxidation in peroxide solution followed by oxide removal in hydrofluoric acid (HF) solution.[1,2] The surfaces treated with HF solution are hydrophobic and quite stable against chemical attacks. It was revealed that hydrogen termination is responsible for the chemical stability of the surfaces.[3–8] However, the hydrogen-terminated surface may be attacked by organic materials already present in the room air. Those materials cannot be completely removed by thermal annealing, and eventually affect the electrical performance of metal–oxide–semiconductor (MOS) devices that are fabricated on the HF-treated Si wafer.[9–14] The origins of undesirable organic contamination are in clean room environments; for example, on walls, the ceiling, HEPA™ filters, storage boxes, carrier boxes, and so on.[13,15,16] To fabricate high-quality, high-reliable MOS devices, therefore, we need an *in situ*, rapid determination of the level of organic contamination on Si wafer surfaces during the fabrication process of the devices.

A number of spectroscopic tools are available for characterizing chemical species on solid surfaces. Among those, infrared absorption spectroscopy (IRAS) is the most appropriate tool to characterize hydrocarbons on Si wafer surfaces. This method has some advantages: First, infrared light that we used as the probing radiation does not significantly deteriorate the outermost layer of the surface. This is because its energy is too low to decompose surface chemical species, especially organic materials such as hydrocarbons. This is in sharp contrast to, for example, electron spectroscopy in which the incident electron beam with high kinetic energies will most likely decompose surface chemical species. Second, IRAS is applicable to the characterization of chemical species on semiconductor surfaces *in atmospheric environments*, and therefore, a specialized ultrahigh vacuum chamber is not required. This makes it possible to monitor *in situ* and in real time the surface chemical state of Si wafers during the fabrication process.

We have now performed an experiment demonstrating the feasibility of infrared absorption monitoring of organic contaminants on a 300-mm-diam Si wafer in the multiple internal reflection (MIR) geometry with modest means. The main purpose of the experiment is to show the detection limit of the present system for organic contamination and then to compare it with the reported upper limit of the contamination level that has no appreciable effect on the electrical performance of MOS devices, that is, 10^{12} carbon atoms/cm^2.[11,13]

A crucial point of this experiment is the alignment of the optical components. The experimental setup we used is schematically illustrated in Fig. 1. 300 mm Si wafers that met the SEMI international standards,[17] were mechano-chemically polished on both sides. The thickness of the wafers was 775 μm. The shape of the wafer's edge is illustrated in the inset of Fig. 1. IR light that emerged from a globar lamp was focused onto the wafer's edge with Al-coated flat and concave mirrors. The concave mirror was aligned so that the IR light was line-focused onto the wafer's edge. The IR light internally reflected about 600 times while going through the wafer. Such a large number of reflections enabled us to

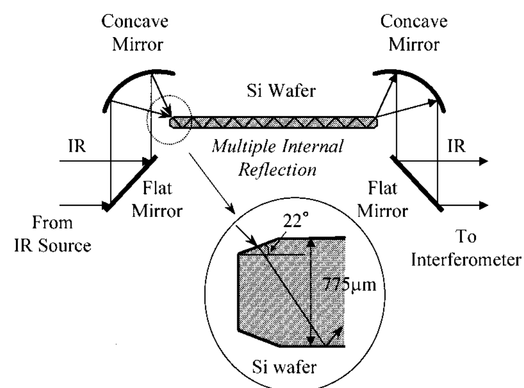

FIG. 1. Schematic of the monitoring system.

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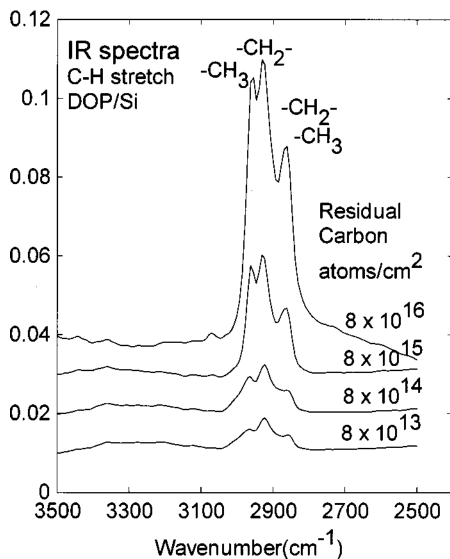

FIG. 2. C–H stretch vibration spectra of the Si wafer surface on which DOP solution was spin coated. The figure attached to each spectrum indicates the surface density of carbon atoms.

monitor traces of surface chemical species. The light that exited the wafer through the edge, on the opposite side, was focused onto a liquid-N_2-cooled InSb detector through an interferometer (BOMEM MB-100). In the present experiment, the resolution of the interferometer was set at 16 cm^{-1}.

The sample surface was initially degreased with acetone solution and then cleaned by exposure to ultraviolet (UV) ozone. Infrared spectra measured for the cleaned surface were used as the background reference spectra. After surface cleaning, dioctyl phthalate (DOP) that was diluted with ethylalcohol was spin coated onto the wafer surface. Recently, it has been reported that DOP is a typical hydrocarbon contaminant on Si wafers stored in the clean room.[13,14,16]

Figure 2 represents typical IRAS spectra in the C–H stretch vibration region for the Si wafer surface on which a diluted solution of DOP was spin coated. The figure attached to each spectrum indicates the calculated density of surface carbon atoms. Since ethylalcohol is quite volatile, we assumed that the C–H vibration bands dominantly originated from DOP. DOP has 24 carbon atoms per molecule, as shown in Fig. 3. We assumed that DOP does not decompose during spin coating, and that all the carbon atoms in DOP remain on the surface. Under these assumptions, we determined the carbon surface density from the DOP concentration of the spin-coated solution and the area of the surface on which the DOP solution was coated. Uncertainties in the surface density thus determined were estimated to be below 20%. All the spectra of Fig. 2 have been collected in room

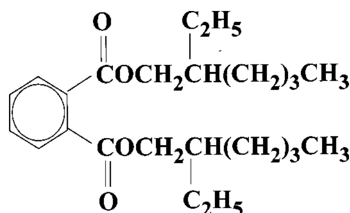

FIG. 3. Molecular structure of DOP.

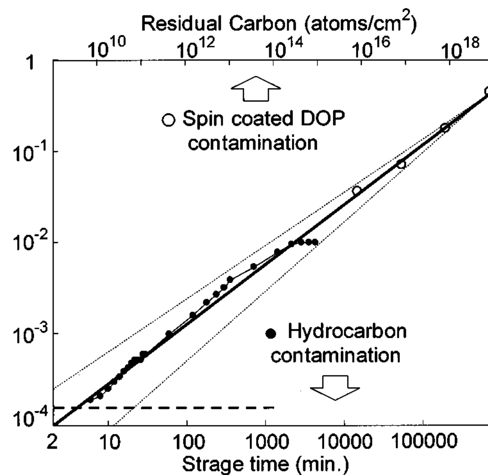

FIG. 4. C–H peak intensity as a function of the surface density of carbon.

air ambient conditions. Three peaks can be clearly identified at 2870, 2930, and 2980 cm^{-1}. The 2870 cm^{-1} peak is due to the C–H stretch vibrations of groups -CH_3 and -CH_2-, the 2930 cm^{-1} peak is attributed to that of -CH_2-, and the 2980 cm^{-1} peak to that of -CH_3. Considering the molecular structure of DOP as shown in Fig. 3, we attribute these peaks to the substituents of DOP.

We plot in Fig. 4 the intensity of the 2930 cm^{-1} peak as a function of the surface density of carbon. A solid line shown in Fig. 4 yields the calibration curve representing the relation between the carbon density and the absorbance of the C–H stretching vibration band. The dotted lines represent errors of the carbon density as determined from the absorbance. In Fig. 4, the dashed line indicates the noise level of the present measuring system. The intersection of the extrapolated calibration curve with the noise level yields the detection limit that is at least below 10^{11} carbon atoms/cm^2. The upper level of carbon contamination required for the fabrication of reliable MOS devices is reported to be approximately 10^{12} carbon atoms/cm^2.[11] The detection limit of the present monitoring system is below this level.

For further demonstration of the feasibility of monitoring carbon contamination on Si wafers stored in room air, we have collected IRAS spectra of a Si wafer surface that was stored in a mini clean booth. The IRAS spectra exhibited quite similar spectral features in the C–H vibration region as with those shown in Fig. 2. The clean booth we used was enclosed with a poly-vinylchloride sheet that contains DOP as the plasticizer. We determine that the observed C–H bands originated predominantly from the DOP that is incorporated in the polyvinylchloride sheet. Indeed, it has been pointed out that DOP may be shed from vinylchloride sheets into the environment.[16] In Fig. 3, the intensity of the C–H absorption peak at 2930 cm^{-1} is plotted as a function of the storage time. We can see from the figure that the contamination level reaches the deterioration level, 10^{12} carbon atoms/cm^2, after only one hour of storage. The present experiment was performed in a simplified mini clean booth. In a dedicated clean room, lower levels of hydrocarbon contamination would be expected since specialized facilities are equipped to reduce contamination originating from the environments. However, for long-term storage in a clean room,

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the wafer surface may be contaminated by significant amounts of hydrocarbon such as DOP. The present monitoring system enables us to detect in real time such traces of hydrocarbon contamination residing on Si wafers that have never been detected by conventional spectroscopic tools.

In summary, an IR monitoring system has been developed for the rapid detection and characterization of organic contamination on 300 mm Si wafer surfaces. IR light propagates through the Si wafer, internally reflecting about 600 times, which makes it possible to detect small amounts of surface contamination on the wafer surface. We found that the present system allows for the detection of hydrocarbon contamination on Si wafer surfaces with a contamination level of below 10^{11} carbon atoms/cm^2.

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