8 Contamination management solutions

8.1 Introduction

In semiconductor manufacturing, i.e. the production of integrated electronic circuits, many crucial process steps are based on vacuum technology. There are several reasons for the use of vacuum technology in Silicon processing:

- Vacuum allows controlled conditions as it excludes the ambient atmosphere from the silicon wafer, namely reactive gases and dust.
- Vacuum allows anisotropic etching of silicon and silicon oxide, the basic process steps for patterning the surface of the silicon wafer.
- Several vacuum based processes allow the deposition of thin layers of all types of insulation and conducting films with controllable properties on silicon wafers.

The development of integrated circuits made from solid silicon is characterized by a steady increase of performance due to an ever increasing number of integrated components per device and shrinkage of the pattern size. In the course of his development the performance of the circuits has doubled approximately every two years since the 1960s which has been predicted by Gordon E. Moore and is known as Moore's law [35]. This has been achieved by a reduction of the smallest structures of integrated circuits like microprocessors and random access memory from about 10 µm in 1970 to sub 0.1 µm after the turn of the millennium. During this period the size of the silicon wafers increased from 1" diameter to 300 mm (~12") to improve throughput and reduce cost.

With the introduction of the 300 mm technology the so called critical dimensions shrank from 150 nm and have reached 22 nm at the time this text is written (2012). With 300 mm wafer size the production technology also changed from open cassettes (Figure 8.2 left) to closed mini environment, i.e. the wafers are transferred from one process equipment to another inside the production site in closed boxes (FOUP = Front Opening Unified Pod, Figure 8.2 right).

Figure 8.2: Wafer handling with cassettes (left) and FOUPs (right)

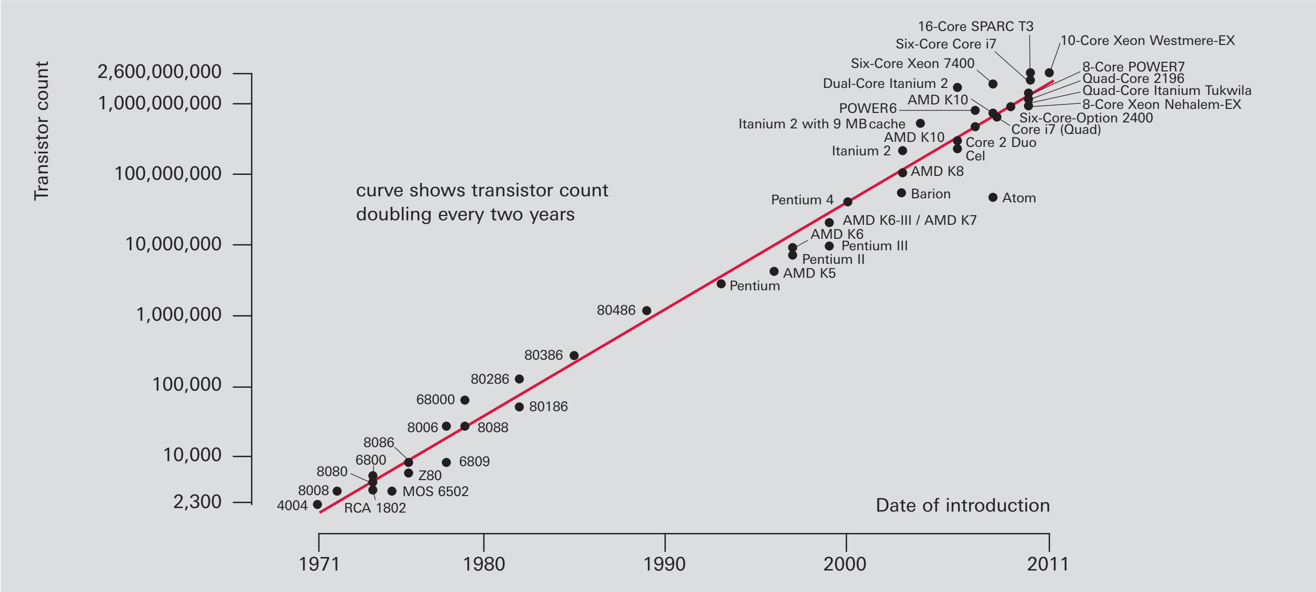

Figure 8.1: Moore's Law (documented by the number of transistors in Intel and AMD microprocessors)

8.2 Contamination

Dust is the natural enemy of integrated circuit manufacturing of small sized devices. In the course of the development of integrated circuits efficient methods have been developed to eliminate dust from the production environment. A dust particle of a size comparable with the elements of the circuit structure (critical dimension, CD) or larger can be problematic if it is accidentally incorporated into the device. A structure of 22 nm of silicon comprises only 41 Si atoms. On this scale not only particles present a challenge but contamination by molecules becomes an increasing challenge. Those contaminations are known as airborne molecular contamination (AMC). The change from open cassettes to closed FOUPs reduced largely particle contamination but at the same time increased the impact of AMC.

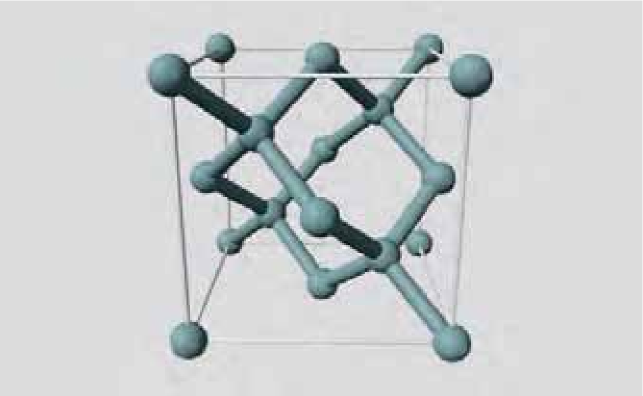

Figure 8.3: Diamondlike crystal structure of Silicon

Molecules on the surface of the wafer which originate from the ambiant air, released from the surrounding surfaces, or from a preceding process step can react with atmospheric gases forming minuscule clusters of reaction products which tend to grow during queue time when wafers are waiting for the next process step. The nucleus of molecular contamination usually is from the many compounds used in semiconductor fabrication.

The International Technology Roadmap for Semiconductors (ITRS) has established a list of AMCs which can provoke wafer defects [36]. This list comprises inorganic and organic acids, bases, sulphur compounds, and volatile organic compounds, see figure 8.4 for details.

There are two main sources of AMC in the FOUPs inner atmosphere. The main source are the wafers stored in the FOUP after each process step. Byproducts from the last process are released from their surface and can be absorbed by the polymer material of the FOUP or reabsorbed on other wafer surfaces. The second source is outgassing from the FOUP, either from the bulk of the polymer or from previously absorbed byproducts of other wafers and/or other processes. As polymers have a high capacity to absorb gases, the FOUP has a "memory" of the wafers it has carried. Compared to these AMC sources the contribution of the well controlled clean room air can be neglected.

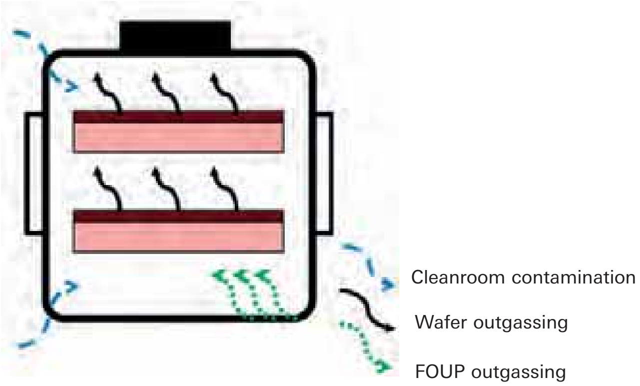

Figure 8.5: AMC Sources in FOUPs

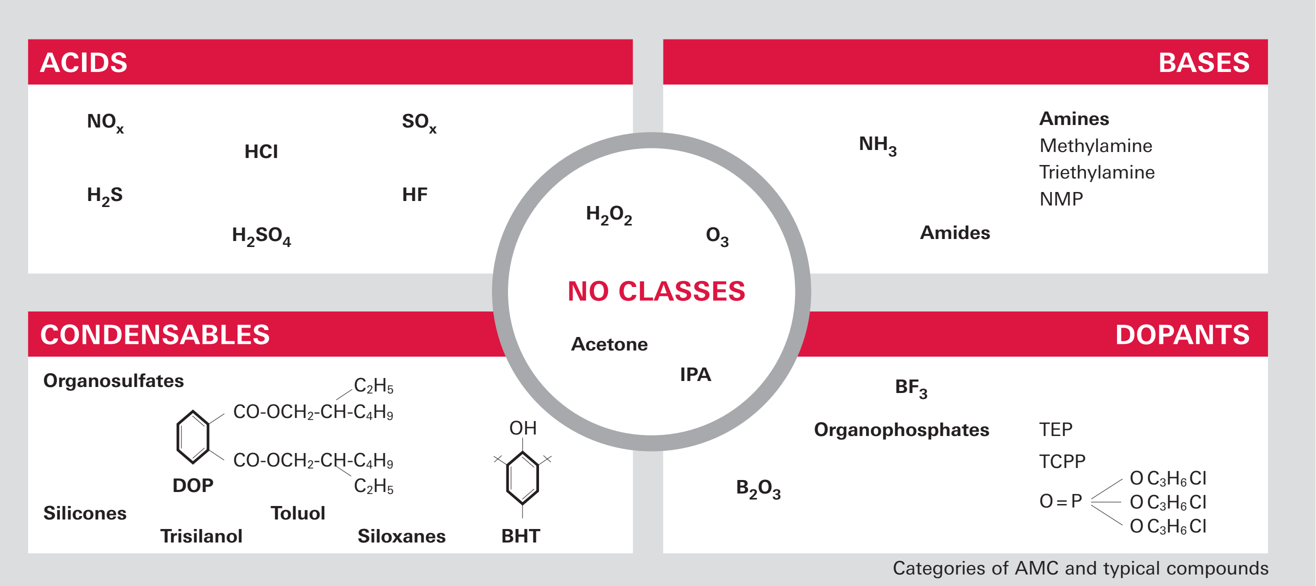

Figure 8.4: Classification of airborne molecular contamination AMC

8.3 The nature of AMC

At atmospheric pressure and ambient temperature a solid surface, which incorporates about 10^{15} atoms/cm^2 receives a flow of incident gas molecules and atoms of the order of 10^{23} [37] per second and square centimeter. This means within nanoseconds the surface will be covered by some layers of gas molecules. The probability of a molecule to stick on the surface depends largely on its nature and the nature and topography of the surface. But even minor traces of reaction by-products in the ppbv range (parts per billion of volume, i.e. 10^{-9}) which hit the surface at a rate of 10^{14} s^{-1} cm^{-2} will cover a surface within seconds if the sticking coefficient is high.

Airborne molecules can be either polar or non polar. In non polar molecules the electrical charges are symmetrically distributed, the centers of positive and negative charges coincide. Examples are nitrogen N_2 or the linear CO_2 molecule. These molecules are kept on a solid surface by weak van der Waals forces, with binding energies typically ranging between thermal energy RT ≈ 2.5 kJ/mol and about 20 · RT. In polar molecules the electrical charges are asymmetrically distributed resulting in a permanent dipolar momentum. Examples for polar molecules are water H_2O and inorganic acids used in semiconductor etching processes like HF and HCl. Binding energies of polar molecules are higher, e.g. for H_2O on a Si(100) surface about 138 kJ/mol. These molecules are likely to interact chemically with the surface, forming nuclei for further reactions.

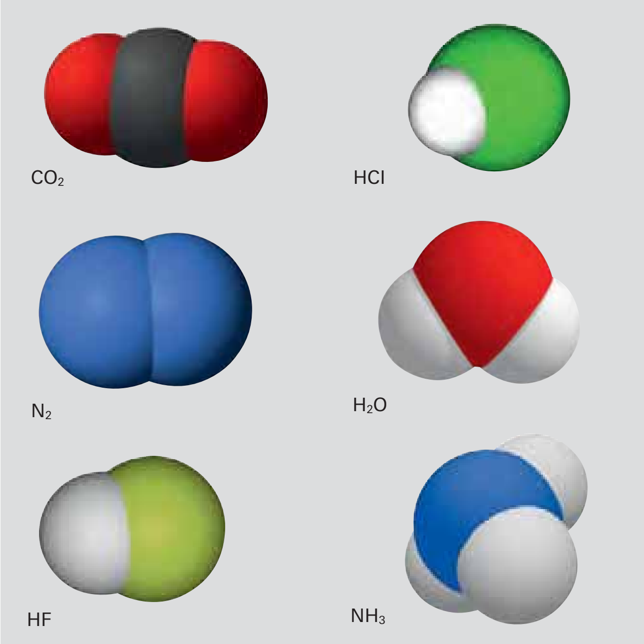

Figure 8.6: Airborne polar and non polar molecules

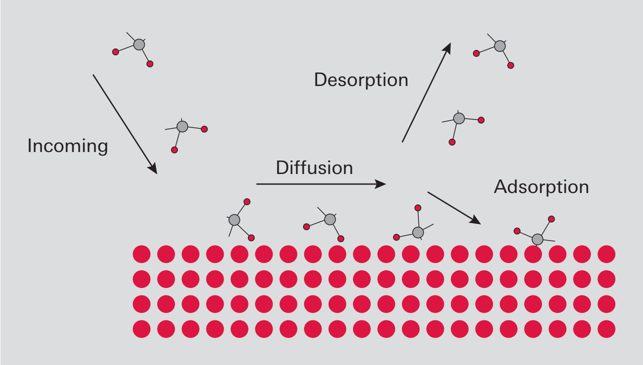

Figure 8.7: Gas-solid interaction at a surface

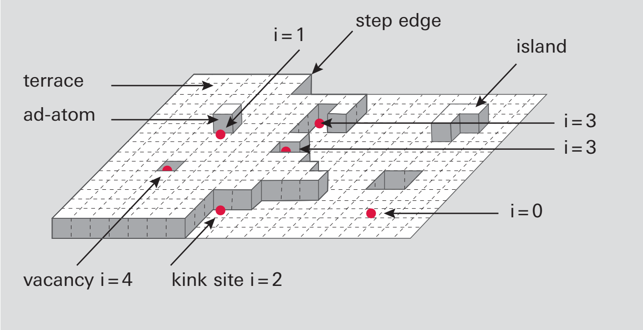

Figure 8.8: Surface sites

8.4 From surface molecular contamination (SMC) to defects

The different phenomena at the interaction plane between a solid surface and a gas are shown in figure 8.7. Gas molecules impinge on the solid, diffuse along the surface, and desorb or get adsorbed to it. A solid surface is the boundary between the bulk material and the outer world. This surface has higher energy than the bulk material because of the pending dangling bonds of the last layer of atoms or molecules. Each of the pending dangling bonds is a potential adsorption site. The free energy of the surface depends on the nature of the material bonds, i.e. metallic, ionic or covalent. The number of adsorption sites increases from well ordered crystal surfaces to polycrystalline and to amorphous polymer materials. Any irregularity increases the number of adsorption sites.

Water vapor plays a special rule in surface processes. At 25 °C and 50 % relative humidity, air contains 16 hPa (1.58 %) of water vapor. Any surface receives a flux of water molecules of about $5 \cdot 10^{21}$ cm^{-2} s^{-1}. In about 200 ns a Mono layer of water could cover a Si (100) surface. Due to the polar nature of the water molecule the first layer will bond tightly to the surfaces and additional layers of water-to-water bonds will form resulting in a stack of water layers. An acid molecule arriving on a surface exposed to atmospheric conditions will meet water molecules to assist in further reactions.
Any material that is capable of absorbing water into the bulk such as plastics or elastomers, will become saturated if it is exposed long enough.

FOUPs are made of polymer materials such as polycarbonate (PC), polyether ether ketone (PEEK), and acrylonitrile butadiene styrene (ABS). These materials can absorb water by 0.12 %, 0.5 %, and 0.7 % respectively which results in water vapour volumes of 6 l, 25 l, and 35 l at ambient conditions. Photo-resist masks are also polymer materials and will absorb water.

Under plasma conditions surfaces receive a flux of gas molecules, energetic ions, and reactive species. Ions help to desorb etching by-products and enhance the etching rate through creation of defects at the surface. After etching the surface is fully saturated with reactive species. A halogenation layer of 1.5 to 2.5 nm has been reported in poly etch with Cl_2 + HBr chemistry [38]. After etching, the wafer surface will release by-products and reactive molecules to the closed environment of the FOUP which, moreover, provides water vapor to facilitate chemical reactions.

From the theory of adsorption and desorption processes the amount of adsorbed gas Θ can be given in the form

$$\Theta = \frac{p \cdot C}{1 + p \cdot C}$$

Formula 8-1: Surface coverage

Where p is the pressure and $C = C(T)$ a function of the temperature. This is known as the Langmuir adsorption isotherm/isobar. An equilibrium coverage Θ_{eq} will establish at a given set of pressure and temperature. The dependence of Θ form p and T is given in figure 8.9. It shows that a low coverage of gas on a solid surface can be achieved by low pressure and high temperature.

Adsorption and desorption are dynamic processes. Non polar molecules have a faster desorption rate due to their lower binding energy. Each non polar molecule leaving the surface offers a new adsorption site. This new site can be occupied by a polar molecule with a stronger binding energy and a lower desorption rate.

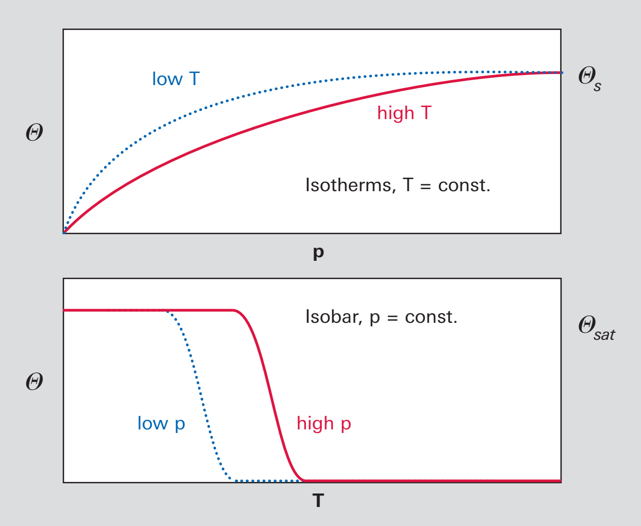

Figure 8.9: Surface after etching

With time, polar molecule concentration will increase at the surface, increasing the probability of defect build up which is a result of the dose D of AMC:

$$D = c_{AMC} \cdot \Delta t$$

Formula 8-2: Dose of contamination

Where c_{AMC} is the concentration of airborne molecular contaminants and Δt the time the wafer surface is exposed to the FOUPs atmosphere.

Figure 8.10: Crystal growth at the edge of a wafer pattern

SMC is at the genesis of crystal growth during queue time. As wafers wait longer for the next process step they receive a higher dose of reactive polar molecules thus increasing the probability of crystals growing to a size which subsequently will generate defects and yield loss.

8.5 Portfolio overview

The dose concept leads to the measures which must be taken to avoid defect generation by AMC:

- Decrease the pressure
- Increase the temperature
- Reduce the time of exposure

As the queue time is a requirement of manufacturing which is needed to assure flexibility in wafer processing, an outgassing of FOUPs and wafers in vacuum at elevated temperatures is the right measure to reduce defects and thus to increase yield. To get control of AMC it is vital to monitor it inside FOUPs and as it is governed by dynamic processes monitoring must be done in the production environment. Pfeiffer Vacuum offers the **APA 302 Pod Analyser** as the appropriate tool for the analysis of AMC. The APA 302 gives information on total acids, total amines, total volatile organic compounds and water vapour on the ppbv level within two minutes. Measurements can be done with empty FOUPs or FOUPs loaded with wafers.

Once AMC has been analysed and its impact on yield identified, appropriate measures have to be taken to improve the situation. To this end Pfeiffer vacuum offers the **APR 4300 Pod Regenerator** as an efficient tool to decontaminate up to four FOUPs in a single run. This patented machine is based on the insights of physical and chemical gas-surface interaction as presented in this chapter. The pod analyser follows a vacuum process as described by figure 8.11. In a first vacuum conditioning step of about five minutes the working pressure is reached. The subsequent purge process desorbs AMC which has built-up on the surfaces and in the last step the FOUP is returned to atmospheric pressure.

The APR 4300 Pod Regenerator has proved its efficiency by yield enhancements up to 7%. New challenges will emerge for semiconductor manufacturing and the dose of airborne molecular contamination will become increasingly important. Therefore alternatives to atmospheric pressure transport between critical production steps have to be developed. Vacuum will surly play an increasing role in future solutions.

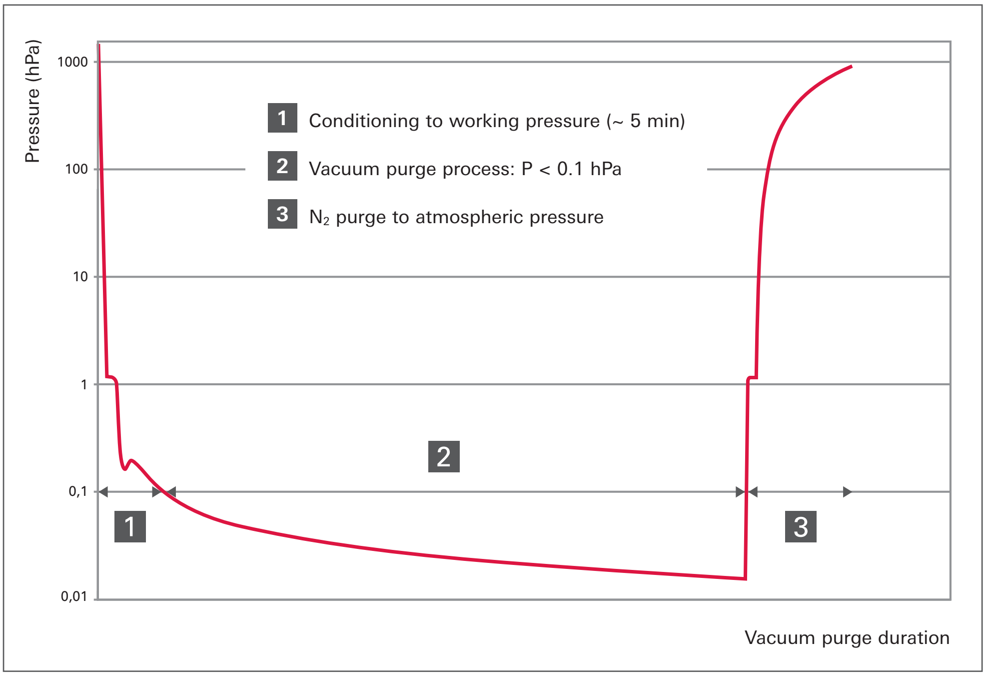

Figure 8.11: Pod regenerator process cycle