TU Clausthal
Clausthal University of Technology

Plasma-oxidation of Ge(100)-surfaces characterized by MIES, UPS and XPS

HL 44.93

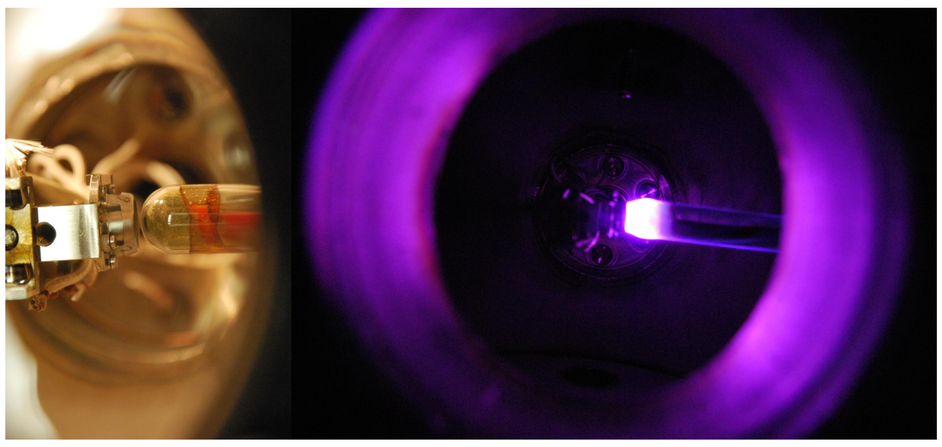
L. Wegewitz[1], S. Dahle[1,2], O. Höfft[3], F. Voigts[2,3], W. Viöl[4], F. Endres[3] and W. Maus-Friedrichs[1,2]

[1] *Clausthaler Zentrum für Materialtechnik, Technische Universität Clausthal, Leibnizstraße 4, 38678 Clausthal-Zellerfeld, Germany*
[2] *Institut für Physik und Physikalische Technologien, Technische Universität Clausthal, Leibnizstraße 4, 38678 Clausthal-Zellerfeld, Germany*
[3] *Institut für Mechanische Verfahrenstechnik, Technische Universität Clausthal, Arnold-Sommerfeld-Str. 6, 38678 Clausthal-Zellerfeld, Germany*
[4] *Hochschule für Angewandte Wissenschaft und Kunst, Fakultät für Naturwissenschaften und Technik, Von-Ossietzky-Straße 99, 37085 Göttingen, Germany*

Introduction

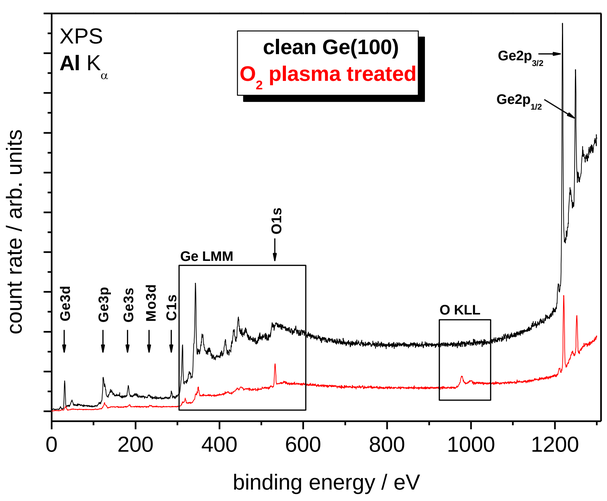
Cleaning and passivation of Germanium surfaces are of tremendous technological interest. Germanium has various applications, for example in complementary metal-oxide-semiconductor elements. The preparation of contamination free Germanium surfaces by methods of wet chemistry turned out to be difficult. Several attempts have been made preparing such surfaces by different plasma treatments [1,2]. We report cleaning and passivation of Ge(100)-surfaces by a dielectric barrier discharge plasma at ambient temperature in oxygen and in air studied by Metastable Induced Electron Spectroscopy (MIES) and Photoelectron Spectroscopy (UPS(He I) and XPS). The plasma treatment is carried out in a preparation chamber which operates up to ambient pressure and is directly connected to the ultra-high vacuum recipient including the analysis equipment. In summary the air plasma treatment as well as the oxygen plasma treatment result in contamination free GeO_2 covered surfaces.

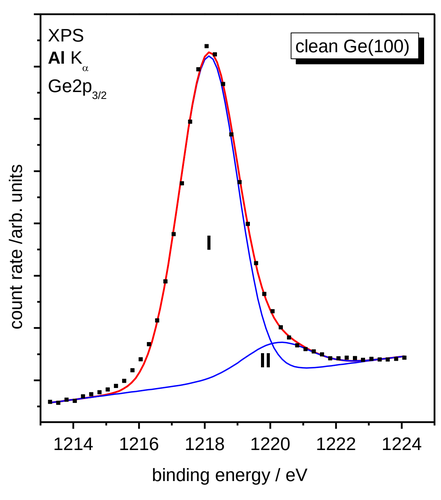
Experimental



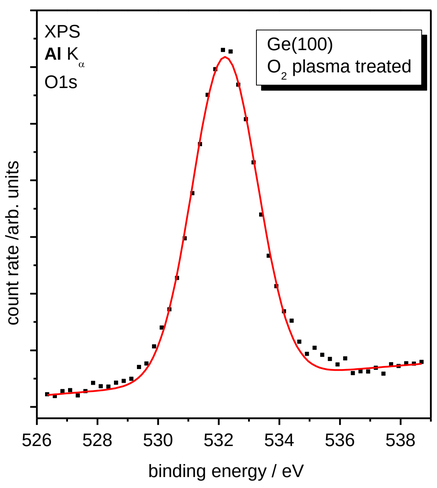
The chemical composition of the clean and oxidized Ge(100) surfaces is investigated by XPS using the AlK_α line (1486.7 eV) of a commercial non-monochromatic X-Ray source (Specs RQ20/38C) and a hemispherical analyzer (VSW HA100). For the determination of the electronic structure near the surface, UPS (HeI, 21.2 eV) and MIES (mainly He* 2^3S_1, 19.8 eV) are applied. All measurements are carried out in an UHV system with a base pressure of about 5.0×10^{-11} hPa.
Samples referred to as “clean Ge(100)” in the following are chemically rinsed by alternately dipping them in HF (48%), deionized H_2O and H_2O_2 (30%). Finally the samples are transferred into the UHV system, annealed at 300°C for 30 minutes and further heated to 500°C (15 min) [3].
The plasma treatments are performed in the preparation chamber (base pressure ~ 5.0×10^{-8} hPa) which is equipped with an electrode for the dielectric barrier discharge and a manipulator for precise positioning of the sample 1 mm apart from the electrode. A high voltage supply generates 11 kV pulses with a repetition rate of 10 kHz and a duration of 0.6 µs. The atmospheres are established by backfilling the preparation chamber with oxygen (Linde 99,995%) or atmospheric air at pressures of 200 hPa and about 950 hPa respectively.

XPS Results



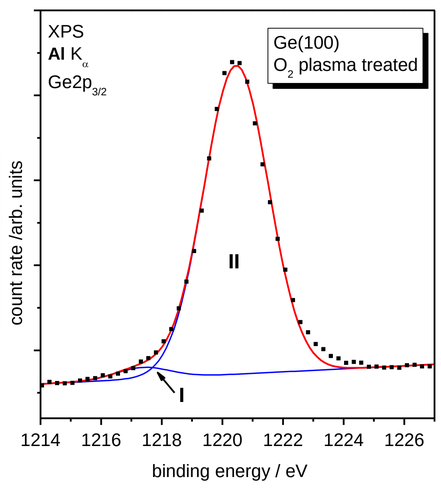


The germanium crystal has been cleaned for the comparison of peak positions and FWHMs with the spectra recorded after plasma treatments. The carbon contamination of the rinsed surface amounts to about 10 %. The oxygen content is below the detection limit.

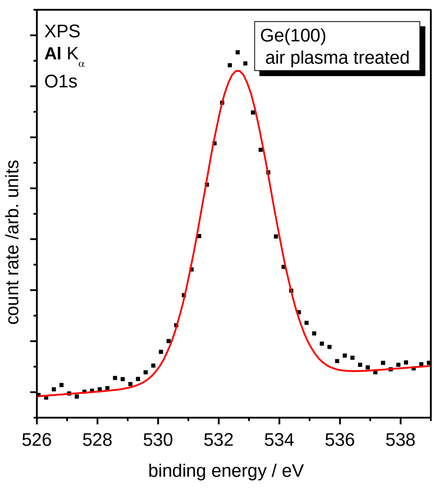


Stoichiometry:

Ge^0	<1.0 %
Ge^{4+}	20.9 %
O	78.4 %
C	<1.0 %

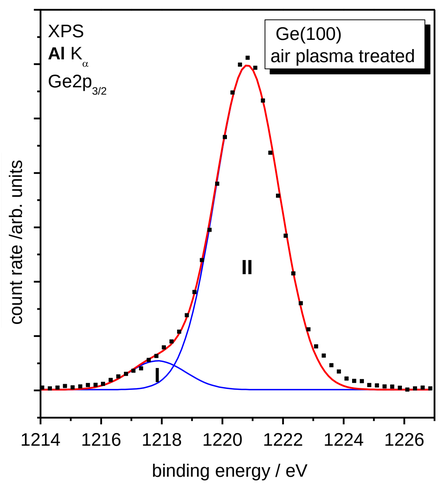


The O:Ge^{4+} ratio amounts to 3.63 after the dielectric barrier discharge in oxygen and to 2.50 in atmospheric air. Obviously the oxygen contents are overstoichiometric. There are no traces of carbon detectable after the plasma treatments, furthermore no nitrogen is incorporated during the treatment in air.



Stoichiometry:

Ge^0	2.2 %
Ge^{4+}	27.9 %
O	69.9 %
C	<1.0 %

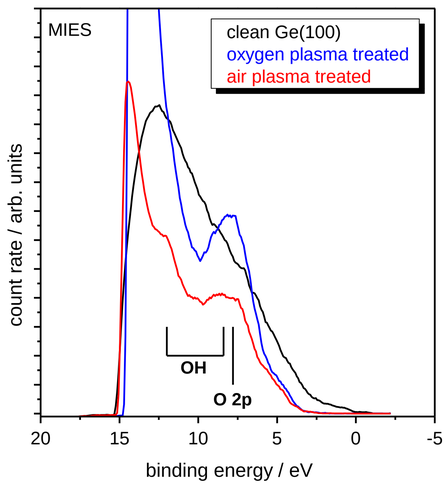


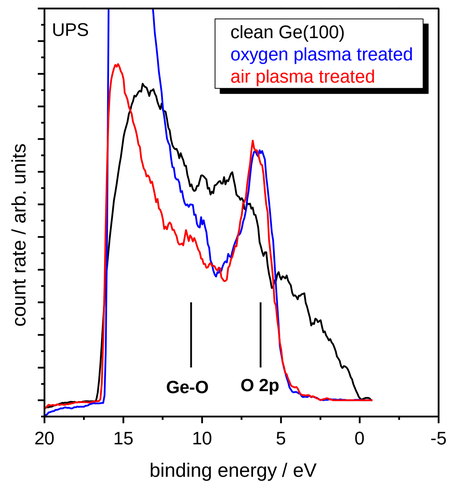
$$d = \lambda_o \cos\theta \ln\left[\left(\frac{D_m\lambda_m}{D_o\lambda_o}\right)\left(\frac{I_o}{I_m}\right)+1\right]$$

D_m atomic density of Ge atoms in the substrate
D_o atomic density of Ge atoms in the oxide layer
λ_m, λ_o inelastic mean free path (substrate / oxide)
θ escape angle of the electrons (10°)

The thickness of the oxide layer after the plasma treatment can be calculated from the intensities I_o and I_m corresponding to the oxide and metal contribution. For the oxygen atmosphere, d amounts to 3.61 nm. Treatments in atmospheric air yield 2.81 nm.

MIES / UPS Results





- The MIES process changes from Auger Neutralization in the case of clean Ge(100) to Auger Deexitation after the plasma treatments.
- MIES and UPS show distinct peaks at 7.8 eV and 6.3 eV respectively which can be assigned to O 2p orbitals.
- The weak contribution at around 10 eV in UPS due to the Ge-O bonds.
- Plasma oxidation in air results in a slight hydroxide contamination of the surface, proven by two contributions at 8.4 eV and 12 eV in the corresponding MIES spectrum.

Summary

- Impurity free GeO_2 covered Ge(100) surfaces can be prepared by plasma oxidation applying a dielectric barrier discharge.
- Comparable results are achieved for treatments in pure oxygen and in atmospheric air.
- The discharge operates in a wide pressure range (5×10^{-4} hPa – 1000 hPa).
- The sample temperature does not exceed room temperature + 10 K [4].

→ Clean and passivated germanium surfaces in one step without sophisticated processes

References

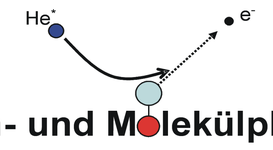
[1] T. Sugawara, and P. C. McIntyre, J. Vac. Sci. Technol. B 24, 2442-2448 (2006)

[2] M. Mukhopadhyay, and C. K. Maiti, J. Vac. Sci. Technol. B 14, 1682-1686 (1996)

[3] K. Prabhakaran, and T. Ogino, Surf. Sci. 316, 1031-1033 (1994)

[4] U. Kogelschatz, Plasma Chem. Plasma P. 23, 1-46 (2003)

Clausthaler Zentrum für Materialtechnik



Atom- und Molekülphysik an Oberflächen