NO₂ sensing properties of amorphous silicon films

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Abstract. The sensitivity to NO₂ was studied of amorphous silicon thin films obtained by e-beam evaporation. The process was carried out at an operational-mode vacuum of 1.5×10⁻⁵ Torr at a deposition rate of 170 nm/min. The layer’s structure was analyzed by Raman spectroscopy, while its composition was determined by X-ray photoemission spectroscopy (XPS). To estimate their sensitivity to NO₂, the Si films were deposited on a 16-MHz quartz crystal microbalance (QCM) and the correlation was used between the QCM frequency variation and the mass-loading after exposure to NO₂ in concentrations from 10 ppm to 5000 ppm. A considerable sensitivity of the films was found in the interval 1000 ppm – 2500 ppm NO₂, leading to frequency shifts from 131 Hz to 208 Hz. The results obtained on the films’ sorption properties can be applied to the development sensor elements.

1. Introduction
Nitrogen oxides (NO and NO₂) are typical air pollutants. They cause acid rain and smog and can also destroy the stratospheric ozone, affect the flora and fauna and lead to problems for human health [1].

In the past few decades, when new types of sensors appeared, a large number of techniques have been developed for environmental monitoring and control of the toxic gases. Among them, the QCM-based techniques attract particular interest due to their high mass-sensitivity. The analytical performance of such sensors strongly depends on the properties of a sensing coating deposited on the QCM electrodes. Semiconductor thin layers, such as SnO₂, WO₃, ZnO, MoO₃, and TiO₂ have been widely investigated for sensing different toxic gases [2]. Many forms of silicon are also interesting materials in the gas sensing field. In particular, porous Si can be successfully used as a sensing coating of chemical sensors for detection of different gases, including NO₂ [3]. The main disadvantage of

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porous Si is that it cannot be prepared as a thin layer by different methods of deposition. A possible alternative is using amorphous \(\alpha\)-Si, which can be prepared as thin layers by standard methods.

The aim of the work is to study the sensing properties to NO\(_2\) of Si thin films by applying the QCM method.

2. Experimental
We used a 16-MHz QCM covered with thin Si films on both sides by e-beam evaporation. The experimental setup is described in detail in [4]. The evaporator consisted of a heated tungsten filament \((I_F=14.5 \text{ A AC})\); cathode voltage \((U_c)\) was applied to the filament and to the screen. The evaporation power necessary for heating the crucible with Si powder is the product of the anode current \(I_a = 75 \text{ mA}\) and \(U_c = -7 \text{ kV DC}\). The evaporation process was carried out at a pressure of \(1.5\times10^{-5} \text{ Torr}\) and calculated evaporation power of \(525 \text{ W}\) at a deposition rate of \(170 \text{ nm/min}\). The as-deposited Si films were characterized by Raman spectroscopy, X-ray photoemission spectroscopy (XPS), and talystep techniques. The Raman spectra were recorded on a Horiba Jobin Yvon LabRAM HR800 spectrometer using a 600 l/mm grating and a HeNe laser for excitation. The thin film samples on glass substrates were placed under the 100X achromatic objective of a BX41 microscope and measured in back scattering configuration. The laser power on the sample was kept below 0.5 mW, so that no heating effects could be observed in the spectra or on the microscope image. The composition and the electronic properties of the Si films were studied by XPS measurements performed on an ESCALAB Mk II (VG Scientific) electron spectrometer with Al radiation \((h\nu = 1486.6 \text{ eV})\).

The sensitivity to NO\(_2\) of as-deposited Si films was measured on a laboratory setup. The methodology of measurements is described in [5]. Dry synthetic air and 1% NO\(_2\) gas were used. The NO\(_2\) concentrations in the test camera were created by changing the ratio of the NO\(_2\) gas and the diluting gas flow. The working temperature was 26±0.2 °C. The QCM frequency was registered by a counter connected to the QCM and to a computer. The measurements can be divided into three stages: purging the Si-QCM structure by dry air until the frequency reaches a constant value, \(F_0\); creating a certain NO\(_2\) concentration and reaching saturation of the frequency value \((F)\); purging the camera with dry air thus restoring the Si-QCM system. The sensing properties of the Si films were estimated by measuring the frequency-time characteristics (FTCs) of the Si-QCM at NO\(_2\) concentrations ranging from 10 ppm to 5000 ppm. According to the Sauerbrey equation [6], the change in the resonant frequency shift \((\Delta F=F_0 - F)\) can be related to the mass change \((\Delta m)\) of the adsorbed gas.

3. Results and discussion
3.1. Properties of as-deposited Si thin films
The spectrum in figure 1 is a typical Raman spectrum of amorphous silicon [7, 8]. The TO-like band is observed at 470 cm\(^{-1}\); the longitudinal acoustic (LA) and the longitudinal optic (LO) regions between 420 and 200 cm\(^{-1}\) and the transverse acoustic (TA) region below 200 cm\(^{-1}\) are also clearly visible. The position of the TO band corresponds to non-hydrogenated amorphous silicon. The full width at half maximum of the peak is 84 cm\(^{-1}\), which is consistent with a comparatively good short-range order. There are no microcrystalline grains, which would give rise to a narrow peak around 520 cm\(^{-1}\). Figure 2 shows the XPS spectrum of the native oxide of amorphous silicon. The photoelectron spectrum exhibits a structure with two well-resolved peaks. The intensive peak at 99.4 eV corresponds to silicon, while the peak at \(\sim102.8 \text{ eV}\) corresponds to oxidized silicon. The latter peak is broad and is decomposed into two peaks using mixed Gaussian-Lorentzian curve fitting. The 103.2 eV peak shows a binding energy similar to that for silicon dioxide (103.4 eV); the peak at 101.6 eV falls in the binding energy range of suboxides (SiO\(_x\) with \(x < 2\)). Thus, the XPS study indicated the formation of a thin layer on the surface of the \(\alpha\)-Si layer containing a mixture of SiO\(_2\), SiO\(_x\), and Si. To estimate the thickness of the SiO\(_x\) layer, we used the quantitative relation proposed by J.M. Hill et al. [9]. The exact estimation is questionable due to the uncertainty in some of the parameters included in this relation, such as the escape depth of photoelectrons emitted from SiO\(_x\) and the intensity ratio of the signals.
from infinitely thick SiOx and Si. There are significant discrepancies in the literature for these values. We used the value of 2.86 nm for the escape depth of Si 2p photoelectrons in SiO2 excited by Al Kα radiation as obtained by K. Takahashi et al [10]. Also, the value of 0.82 for the intensity ratio of infinitely thick SiOx and Si was taken from the work of M. F. Hochella et al. [11] for Si2p spectrum excited by Al Kα radiation. Using these values we calculated the oxide layer thickness to be 2.1 nm.

Figure 1. Raman spectrum of a Si film.

Figure 2. XPS spectrum of a Si film.

3.2. Gas sensing properties to NO2 of the Si films
The gas sensing properties of α-Si were measured by a consecutive increase of the NO2 concentration after the saturation process, because of the low unloading rate of the Si-QCM system. A considerable initial layer sensitivity was detected at 1000 ppm NO2.

Figure 3 shows the response of a Si thin film to 1500 ppm NO2 concentration. Three regions can be distinguished: the first one indicates a quick response, the second one, a slower response, and the third one is the unloading region after the saturation process. While in the first 52 s F changes by 21 Hz, in the next 68 s it decreases by only 6 Hz, i.e. the sorption rate decreases from 24 Hz/min to 5.4 Hz/min.

Figure 3. FTC of a Si-QCM structure.
Si thickness – 174 nm, NO2 – 1500 ppm.

The presence of two sorption stages proves that the process is limited by the layer’s surface and its thickness. The desorption process in the third region proceeds slowly. Comparing the first region of sorption with the desorption region for a period of 52 s points to a desorption rate lower by a factor of
three than the sorption rate (9 Hz/min). The low desorption rate is caused by the quantity of sorbed mass on the layer and its depth.

Recovering the frequency by scavenging the system showed that the sorption has a physical character. Figure 4 illustrates the response of the Si films to different (1000 – 2500 ppm) NO\textsubscript{2} concentrations. After treating the system by NO\textsubscript{2} (1000 ppm), a rapid decrease of the frequency shift was registered. The consecutive increase of the NO\textsubscript{2} concentrations in the flow after the processes of saturation showed a considerable decrease in the frequency shift. The $\Delta F$ for each NO\textsubscript{2} concentration was calculated.

Figure 5a demonstrates the linear character of the dependence obtained. In the interval studied of 1000 – 2500 ppm, $\Delta F$ changed (131 Hz - 208 Hz) and the sorbed mass of NO\textsubscript{2} was calculated correspondingly. The dependence is shown in figure 5b. The sorbed mass is increasing linearly from 29,13 ng to 46,26 ng when $\Delta F$ changes from 131 Hz to 208 Hz.

Figure 5. Frequency change (a) and mass-loading (b) of Si-QCM vs NO\textsubscript{2} concentration.

Conclusions
Si thin films were prepared by e-beam evaporation. The results obtained showed that the layers are amorphous with a thin SiO\textsubscript{x} films existing on their surface. The layers possess high sensitivity in the interval 1000 – 2500 ppm NO\textsubscript{2}. The process of sorption is physical, so that the response times are short. The Si investigated in the Si-QCM structure could be used as sensor element for NO\textsubscript{2} detection.

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