Photocatalytic decomposition of methylene blue via Fenton mechanisms by silicon wafer doped with Au and Cu: a theoretical and experimental study

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Abstract In this work, we studied the photocatalytic and the structural aspects of silicon wafers doped with Au and Cu submitted to thermal treatment. The materials were obtained by deposition of metals on Si using the sputtering method followed by fast heating method. The photocatalyst materials were characterized by synchrotron-grazing incidence X-ray fluorescence, ultraviolet-visible spectroscopy, X-ray diffraction, and assays of H_2O_2 degradation. The doping process decreases the optical band gap of materials and the doping with Au causes structural changes. The best photocatalytic activity was found for thermally treated material doped with Au. Theoretical calculations at density functional theory level are in agreement with the experimental data.

Introduction

The textile industry is among the most important sectors of industrial activity. The environmental impact caused by this industry is due to the large production of wastewater containing organic contaminants. These compounds change in biological cycles, particularly in the photosynthesis process [1]. The decomposition study was done with a basic dye as a model molecule: methylene blue [2, 3].

Advanced oxidative processes have been an important alternative in wastewater treatment, those processes are based on the hydroxyl radical ($^\bullet$OH), which is capable of causing degradation of the organic compounds. The $^\bullet$OH can be produced by several semiconductor materials under light irradiation, through the decomposition of H_2O_2 molecule [4]. Reactions involving hydrogen peroxide decomposition catalyzed by materials to generate the $^\bullet$OH radical, have received special attention due to the advantages in relation to the classic homogeneous process involving iron soluble salts (Fenton reaction) [1]. These advantages are: (i) it is a heterogeneous system, facilitating all the operations in the treatment of the effluent; (ii) it operates in neutral pH, thus avoiding the need for acidification stages (pH 3) or further neutralization, thus preventing the generation of sludge; and (iii) the system can be recycled/regenerated by reducing the surface Fe^{3+} species.

In this work, we have investigated the effect of doping Si-wafer with Au and Cu, on photocatalytic activity in the H_2O_2 decomposition. The Si-wafer was chosen because it has been a widely studied material and therefore, well-known in the literature. Targeting a better understanding of the experimental data, theoretical calculations were carried out at the Density Functional Theory (DFT) level.

Experimental

Sample preparation

The photocatalyst materials were obtained through the introduction of contaminants in high pure silicon (111) crystal.

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Thin films (10 nm) of Cu and Au were deposited on silicon substrates by DC sputtering, using a Balzers BA-510 instrument. We used a base pressure of 2×10^{-7} mbar before deposition.

Theses samples were submitted to thermal treatment for 1 s at 700 °C, using a rapid thermal processing system (RTA AG Heat Pulse 410), in an argon atmosphere. A set of non-annealed samples were preserved as a reference. After annealing, the metallic films were removed by chemical etching. Only Cu and Au atoms buried in Si substrate remained.

Sample characterization

The grazing incidence X-ray fluorescence (GIXRF) measurements were performed in the XRF Beam Line at the synchrotron facility of the Brazilian Synchrotron Light Laboratory (LNLS). The radiation is emitted by a bending-magnet installed in the storage ring. The incident beam was monochromated by Si crystal channel-cut, and the photon count was normalized by an ionization chamber. The Ge hyper purity EDX was used as the fluorescence photon detector. The samples were put in a sample-holder, which was coupled to a goniometer. The monochromatic beam incident on samples was 12.5 keV, and the range of scanning angles were 0–1 degrees (Fig. 1).

The UV-vis spectrum was recorded by a Cary 500 Scan spectrophotometer. The absorption (a/S) data was calculated from the reflectivity using the Kubelka–Munk transformation. Practically, optical gaps are determined after a Kubelka–Munk transformation of the reflectivity spectrum as the intersection point between the energy axis and the line extrapolated from the linear portion of the absorption threshold [5].

The X-ray diffraction (XRD) patterns were measured at room temperature using a Siemens D5000 X-ray diffractometer. The Cu$K\alpha$ with $\lambda = 0.154$ nm was used as the X-ray source.

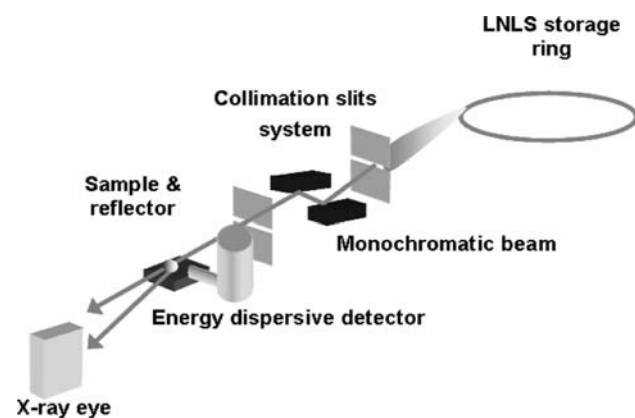**Fig. 1** Experimental setup for performed TXRF measurements

Photoactivity measurement

We employed two ways to analyze the photoactivity performance of Si-wafers doped with Au and Cu. The first was to measured in terms of the H_2O_2 degradation in a $1.6 \times 1.6 \times 3.0$ cm glass tube microreactor. One piece of the square Si-wafer was placed in the microreactor with 1 mL of H_2O_2 20% (v/v) solution, and the tests were performed in visible light. The photocatalytic activity was determined by measuring the amount of H_2O_2 degraded, through the volume of O_2 liberated [2].

The other form was the photocatalytic activity experiments, where the degradation of methylene blue was observed. The measurements were carried out with 0.1 mL of hydrogen peroxide, H_2O_2, solution (20% v/v) (Merck) and 5 mL (25 mg L^{-1}) of methylene blue (Petroquímios), at pH 7.5, in a microreactor made of glass tube with $4 \times 3 \times 3$ cm, which was put on a square piece of Si-wafer. The degradation of methylene blue solution was evaluated under constant agitation, visible light, and all reactions were carried out at 25 °C. We removed aliquots from the six systems at intervals of 15, 30, 60, 90, and 120 min; and dye photodegradation was monitored by measuring the absorbance at 665 nm with a Shimadzu UVPC 1600 spectrophotometer (UV/Vis).

Theoretical calculations

All calculations were carried out using the Gaussian 03 program package. The hybrid density functional method B3LYP, which includes Becke's three parameter non-local exchange functional with the correlation functional of Lee–Yang–Parr was used for this investigation [6]. The effective-core-potential LANL2DZ basis set was used for the atoms of Au and Cu. The atom of silicon was described by SDD basis set. For H and O atoms, the standard 6-31G(d) and 6-31++G** basis set were used, respectively. This computational procedure has been employed previously on similar systems with success [7].

The structure of $Si_{16}H_{24}$ cluster model was fully optimized without any constraints. From this theoretical methodology, we investigated the interaction of hydrogen peroxide with the cluster containing Au and Cu adsorbed on two different sites, for a variable distance of the peroxide.

Results and discussion

Silicon is a quite commonly studied semiconductor material, however, the relationship between depth profile and photocatalytic activity is not well understood so far. Figure 1 shows the sample employed in this work; according

to this procedure, we attempted to obtain samples with peculiar distribution of the dopant below the surface of the Si-wafer. After removal of the films, the samples were submitted to GIXRF measurements.

The GIXRF is a non-destructive method capable of investigating the depth-profiling and buried residues, which is a variant of TXRF. It is based on gradually tilting the sample near the critical angle of total reflection [8]. In the GIXRF a monochromatic and collimated beam enters the sample at a low angle, usually a few degrees. Due to the index of refraction of X-rays the beam is totally reflected if incident angle is smaller than critical angle for the surface. In this region the penetration depth is about 3 nm. Due to the raise in the critical angle, the penetration depth becomes more elevated. Increase in the incident angle originate increases the penetration depth. The incident beam reaches the atoms buried inside the substrate, which emitted fluorescent photons. The fluorescence intensity is proportional to the depth. The mathematical reason for this phenomenon is well-known: it is possible to simulate curves and foresee what the depth of the atoms located inside is.

To determine the depth parameters, theoretical calculations of fluorescence intensity were compared with the experimental data. This was achieved by fitting the theoretical curves to the experimental depth-profiling data. The depth diffusion was determined using the computational facility, which has been under development at XRF beam line LNLS. The software executes the calculations, simulating the fluorescence intensity curves in function of the incidence angle so that the software generates theoretical curves of fluorescence intensity in function of an angle. Figure 2 shows the intensity fluorescence curves versus angle reported in the experimental data and the fitting curves given by the equation are already mentioned.

The fitting curves show that in both samples, diffusion of dopants occur into the Si-wafer. The diffusion is larger for samples that were submitted to a thermal treatment, as expected.

An interesting fact was observed with Au, because this element was found at a greater depth than with Cu. For Si–Au–RT and Si–Au–700, the experimental data suggest that the atoms are buried from 7 to 9 nm and 47 to 55 nm, respectively. Turning to the Si–Cu–RT, we observed the atoms at 2–4 nm and for Si–Cu-700 at 35–41 nm. Hence we had four kinds of materials with different depth profiles. According to the literature data, Au does not react very well with silicon under these conditions, so Au atoms were free for migration into the Si-wafer. However, Cu atoms can react with silicon forming copper silicides, such as Cu_3Si and Cu_4Si. In line with that, since Cu reacts, its mobility might be less expressive than Au's mobility [9]. This hypothesis is in agreement with the experimental data, and the Au atoms had a higher mobility in the Si-wafer.

Fig. 2 Experimental and theoretical fitting data of fluoresence intensity versus angle scan for Au and Cu diffused in Si-wafer. In the chart RT = room temperature
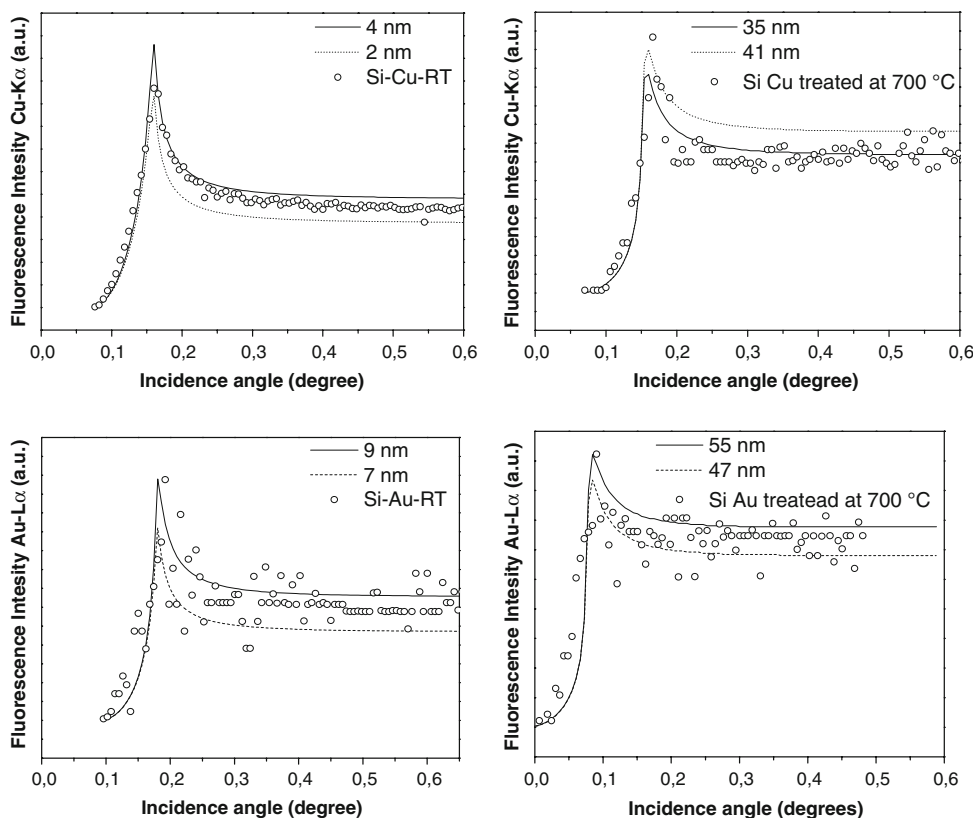
The XRD spectra (Fig. 4) allowed the observation of a different behavior for Au and Cu in Si. The Si-wafer doped with Cu does not present any new signals when compared with high pure Si-wafer. On the other hand, Si-wafers doped with Au showed three new signals at 2θ 27, 39, and 59. The signal at 2θ 27 is the characteristic of rombohedral silicon oxide [10]. As for the signals at 2θ 39 and 59, one question arises due to the existence of signals of silicon oxide triclinic in this region. In addition, there are also signals that correspond to gold oxide, more precisely 2θ at 36 and 60 [11, 12]. Therefore, it is difficult to determine with accuracy which phase corresponds to those signals, since an overlap of signals might happen. The thermal oxidation of silicon bulk forming SiO_2 in presence of oxygen could occur around 630–750 °C, and we believe that Au could decrease the energetic barriers for this transformation, such as what happened when Cr is present on Si surface [13].

From UV-vis spectra, we could observe slight shifts in the positions of the bands due to a small amount of dopant. This suggests that the doping changed the optical propriety of materials.

The values for the energy band gap were calculated; in this case, we focused on the smallest band gap for Si–Cu-700 (0.50 eV) followed by Si–Au-700 (0.63 eV). In the literature, there are works studying effects of reflectivity properties of Si-wafer submitted to thermal treatment, fundamentally thermal treatment causes more disorder in solid structure, and this could lead to reduction in the band gap energy [14]. Although, in this work, we observed that that effect on silicon structure is not a crucial factor. Whereas the material based on Si–Au was better scattered and diffused more deeply than the Si–Cu materials, the Si–Cu materials presented smaller band gap values. We are studying a surface phenomena, so the dopant atoms under large distance seem not to meaningfully influence the band gap. In this way, the band gap might be a function of the blend among the insertion of defects and dopant [15].Therefore, every Si-wafer doped material presented a band gap less high than pure Si-wafer, which was 1.15 eV.

The decomposition capacity H_2O_2 was measured by an indirect approach, evaluating O_2 formation in a Fenton-like mechanism. The Fenton reaction ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$), involving hydrogen peroxide and Fe^{2+} in solution, is used to degrade contaminants, such as textile dyes, present in the industrial waste waters. In order to minimize the amount of the ferric hydroxide sludge formation in this homogeneous reaction, some iron oxides such as magnetite (ideal formula, Fe_3O_4), and hematite (α-Fe_2O_3), have been used instead of Fe^{2+} solutions [16, 17]. The active heterogeneous redox processes are increasingly replacing the homogeneous systems in the catalysis research [18–26] and in some technological
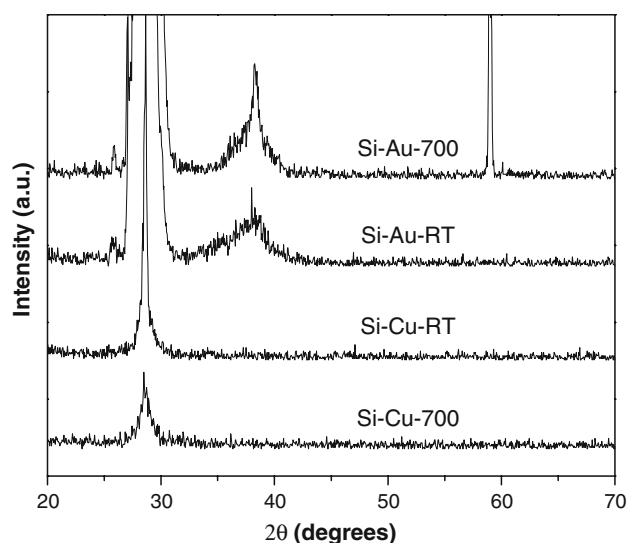

**Fig. 3** Scan XRD patterns of the doped wafers

applications, such as in environmental remediation, as the solid species are easier to be removed from the reaction medium, being more easily recycled. In some cases, solid catalysts present better catalytic performance than their homogeneous counterparts (Fig. 3).

Figure 4 (left panel), shows that Si–Au-700 was a better material for this reaction, followed by Si–Cu-700. The results for the materials not submitted to thermal treatment were similar to those results with pure Si-wafer. So, it is clear that the increase of defects in the structure had an important role in this activity. As it is, the Si–Au-700 activity was two times higher than Si–Cu-700. Many factors could explain this result, such as extension of defects, and the affinity of H_2O_2 for Au or Cu in the structures.

In recurrences of results obtained for H_2O_2 decomposition, we evaluated the capacity of the Si-wafer material to be employed in the degradation of methylene blue. In the literature, methylene blue is often used as a model compound.

The Fig. 4 (right panel), shows the curves of absorbance obtained during the degradation experiments of methylene blue. We could explain that it resembles the H_2O_2 decomposition patterns, which was expected, and probably the degradation of the organic dye takes place by radical reaction. Since the wafer material decomposes the H_2O_2 forming hydroxyl radicals, these follow, reacting with methylene blue. As in the decomposition experiments, the better material was the Si–Au-700, followed by Si–Cu-700, and this could be more an indication that the degradation of methylene blue occurred by reaction with hydroxyl radical, obtained by degradation of H_2O_2 in the surface of Si-wafers. This kind of reaction between methylene blue and H_2O_2, has been studied in the literature [3]. We also observed one small decrease in absorbance of methylene

Fig. 4 Profile of O$_2$ liberation, obtained by H$_2$O$_2$ degradation catalyzed by Si-wafer doped materials
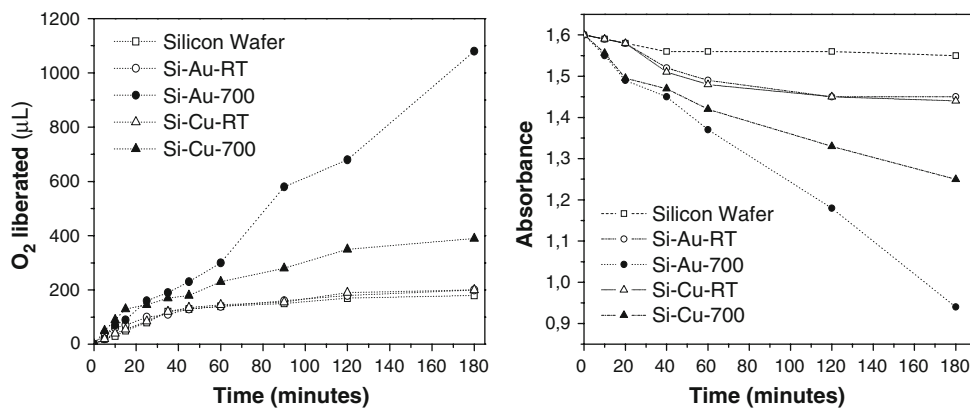
blue in the Si-wafer non-doped with metal, and in this case the decrease in absorbance can be attributed to adsorption phenomena of methylene blue in the surface of the wafer. The Si–Au-700 and Si-Cu-700 were tested in reaction 5 cycles; we did not observe any loss of activity.

Theoretical calculations were carried out in order to rationalize the experimental results. We simulated the approximation of H$_2$O$_2$ to the silicon surface doped with Au and Cu in two singular sites (Fig. 5).

The energies calculated for this system are presented in the Fig. 6. The Si-wafers doped with Au lead to a smaller energy when they interact with H$_2$O$_2$ than wafers doped with Cu. These results are in agreement with the experimental data of H$_2$O$_2$ degradation. We do not observe relevant differences among the approximation sites. Liu and co-authors studied a similar situation [7], in which Cu and Au interact with the silicon surface and according to those researchers the Au presents lower energy in consequence to the relativistic effects. Because of the relativistic effect of Au atom, the energy of orbital 5d increases and that of orbital 6s decreases, and the energy gap between them is very small, therefore the interaction between

Fig. 5 Silicon clusters. The upper panel shows the approximation of H$_2$O$_2$ in distinct sites of contaminated clusters. The lower panel shows the pure silicon, solid line is the A site, and dash is the C site
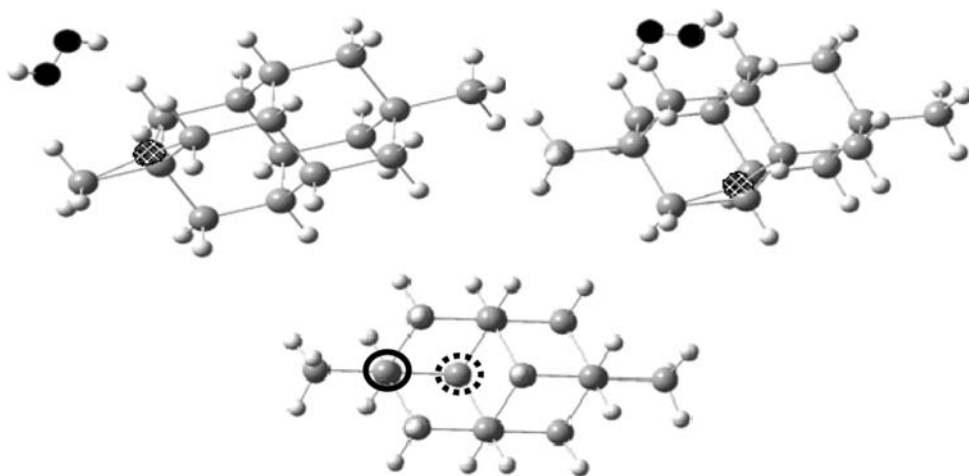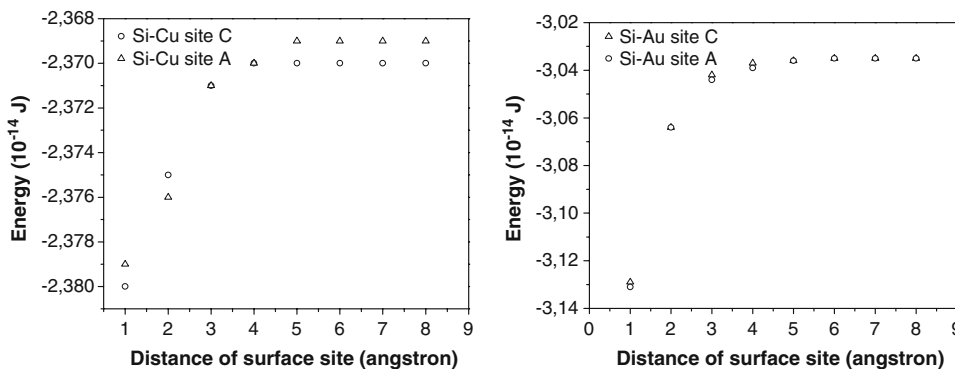
Fig. 6 Potential Energy Curve obtained by interaction among silicon clusters contaminated with Au and Cu, in two distinct sites of clusters are denoted as "site C" and "site A"

electrons of the Au dopant and silicon decreases the energy of the whole cluster [7]. In this way, the wafer doped with Au presents lower energy; so the interaction with H_2O_2 occurs at a lower interaction energy. Such a fact certainly would cause H_2O_2 to move more easily towards the silicon surface, and this phenomenon is fundamental for degradation to take place.

Conclusions

The Si-wafer had its optical and structural properties modified by doping process. The GIXRF measurements shows that Au atoms self diffuse easier into silicon and a thermal treatment strongly increases this diffusion. The doping significantly reduces the band gap, hence smaller energy values were found for Si–Cu, though these materials presented less diffusion into silicon structure. DRX data indicated the possibility of SiO_2 formation, but just in materials doped with Au. Photocatalytic tests show Si–Au-700 is a better material, and its activity was attributed to an increase of defects in structure and affinity with H_2O_2 molecule according to theoretical calculations. The degradation test of methylene blue shows the best activity for Si–Au-700, followed by Si–Cu-700, in agreement with tests of H_2O_2 decomposition, and this indicates that the most probable way for degradation of methylene blue was the reaction with the hydroxyl radical produced during H_2O_2 decomposition. Theoretical calculations at DFT level demonstrated smaller interaction energy values among structures doped with Au and H_2O_2, and this fact help us to rationalize the experimental data. Thus, we may conclude that the Si–Au-700 activity is due to defects in its structure in combination with the affinity of H_2O_2 with cluster contaminated with Au.

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