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Microstructured adsorbent material: silica dioxide - polyaniline for retaining aniline and chromium ions

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The alkaline etch (KOH) of silicon is one of the well-known methods for obtaining integrated circuits on silicon (chips), but the resulted alkaline solution of potassium silicate is a waste. This paper presents a recovery method of potassium silicate alkaline solution by its transformation in a microstructured adsorbent material for aromatic amine derivatives and chromium ions. The micro-structured adsorbent material is obtained by mixing the potassium silicate alkaline solution with an acidic solution of polyaniline, which is obtained by the oxidation of aniline hydrochloride with potassium persulphate. The silica-polyaniline (SiO_2-PANI) micro-structured material was characterized in terms of morphology (SEM, HR-SEM), structure (EDAX, FTIR) and its process performances (adsorption of anilines and chromium ions). The results show that silicon for electronic use can be fully exploited, both as integrated circuit and as adsorbent material for aniline or chromium ions, presenting economical, technical and environment protection benefits.

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1. Introduction

World production of silicon amounted to several hundred thousand tons, but only about 5,000 tons is pure silicon (99.99%) used in microelectronics [1]. There are several etching procedures to make the circuits on silicon [2-5], but the alkaline corrosion with potassium hydroxide is the most versatile method for chemical etching [6-8]. The chemical corrosion in alkaline media has grown thanks to the possibility to tailor the shape of the silicon crystal (anisotropic etching), and the facility offered by the alkaline solution in which various substances for acceleration, moderation, or even for corrosion's control could be dissolved [9, 10]. However, applying this method significant quantities of alkaline potassium silicate solutions are produced (in particular) that provoke undesirable environmental impacts, and huge losses of pure silicon [11,12].

This paper presents a recovery method of the alkaline potassium silicate solution resulting from the alkaline etching of silicon, through a transformation into an adsorbent material for aromatic amine derivatives and chromium ions.

The adsorbent material has been obtained by mixing the alkaline potassium silicate solution with an acidic solution of polyaniline resulted from the oxidation of aniline hydrochloride with potassium persulphate. The silica-polyaniline micro-structured material was characterized in terms of morphology (SEM, HR-SEM), structure (FTIR, EDAX) and performance process (adsorption of aniline and toluidines, and the retention of chromium ions from phosphate solutions). The results show that silicon for electronic use can be fully exploited, so that as integrated circuit and as adsorbent material, with beneficial effects on the environment.

2. Experimental

2.1 Materials

There were used silicon wafers (Topsil, Denmark), hydrochloric acid (Sigma Aldrich), potassium dichromate (Merck), potassium hydroxide (Riedel - deHaen), aniline, o- and p-toluidine (Merck), potassium persulphate - $K_2S_2O_8$ (Merck) and distilled water. The quartz fiber filter (grade QF) with diameter 47 mm, were purchased from Frisenette ApS, Denmark.

2.2. Methods

Into one liter etching autoclave, equipped with thermostat and adapters for hydrogen collection [6], there were introduced 500 mL of potassium hydroxide 40% and 10 silicon wafers. After about 4 hours of etching, monitored by the amount of the hydrogen released, the resulting alkaline solution (SI) is collected in a 2 L vessel. Separately, it was dissolved into 1L vessel, 50 mL of aniline in 250 mL 37% hydrochloric acid solution, then added 200 mL of 1 M potassium persulphate. After 4 hours, the acidic solution (SII) is thoroughly mixed, in drops, with the alkaline solution (SI). A brown precipitate was obtained and then it was filtered in portions of 100 mL suspension.

The quartz filters of 47 mm diameter were used in a Sartorius funnel. The precipitate was afterwards washed with distilled water four times and it was subsequently dried 48 hours in a vacuum heating cabinet at 105°C.

The quartz filters with silica - polyaniline nanomaterial were weighed and then placed in a capture module for aniline vapors (Fig. 1).

a *b* *c*

Fig. 1. View of the adsorption module for aniline: a - overview; b - components of the module; c - fixing the adsorbent material.

The used module allowed simultaneous testing of five filters with adsorbent material, so that the adsorption results represent an average of the obtained values for the aniline, o-, m- or p-toluidine retention.

Determination of the adsorption capacity was achieved using a gravimetric method by help of a balance KERN type ALT 220-4 NM. The quartz discs were weighed before (W_c), after the retention of the adsorbent material (W_m) and after the aniline adsorption (W_a), so that the adsorption capacity of aniline (C_a) was determined by formula (1):

$$C_a=(W_a-W_m)/(W_m-W_c)\,[g_{aniline}/g_{adsorbent\ material}] \qquad (1)$$

The retention of aniline (R_a%) was determined using equation (2):

$$R_a(\%) = [1 - (C_{af} - C_{ae}) / C_{af})\ x100 \qquad (2)$$

where: C_{af} - the aniline concentration in feed, and C_{ae} - the aniline concentration in effluent.

The determination of aniline is carried out by a spectrophotometric method described previously [13], using a spectrophotometer CAMSPEC.

The retention of chromium ions (R_{Cr}%) is determined using equation (3):

$$R_{Cr}(\%) = [1 - (C_{Crf} - C_{ae}) / C_{Cf})\ x100 \qquad (3)$$

where: C_{Crf} - the aniline concentration in feed, and C_{Cre} - the aniline concentration in effluent.

The determination of chromium ions was done by atomic absorption spectrometry using a Perkin Elmer AAS. The scanning electron microscopy (SEM) and EDAX analysis were performed with a FEI instrument (FESEM Hitachi S4500). The materials were also characterized through FTIR analysis. The FT-IR spectra were obtained by help of Bruker Tensor 27 Instrument with diamond ATR.

3. Results and discussion

3.1. Material synthesis

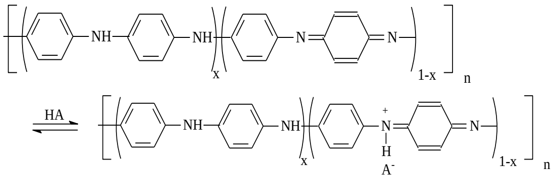
The silicon wafers' chemical etching with potassium hydroxide applied to obtain the integrated circuits (chips) involves a reaction (4) which transforms silicon into potassium silicate by releasing hydrogen [6-8]:

$$\mathbf{Si + 2H_2O + 2OH^- \rightarrow SiO_2(OH)_2^{-2} + 2H_2\uparrow} \qquad (4)$$

The alkaline solution (SI) could be transformed into silica (SiO_2) through its neutralization.

For neutralization it was used an acidic solution (SII) which was obtained as hydrochloride after the aniline oxidation with potassium persulphate according to reaction (5) leading to polyaniline (PANI) [14,15]:

$$\mathbf{C_6H_5\text{-}NH_3\ ]^+Cl^- + K_2S_2O_8 \longrightarrow}$$

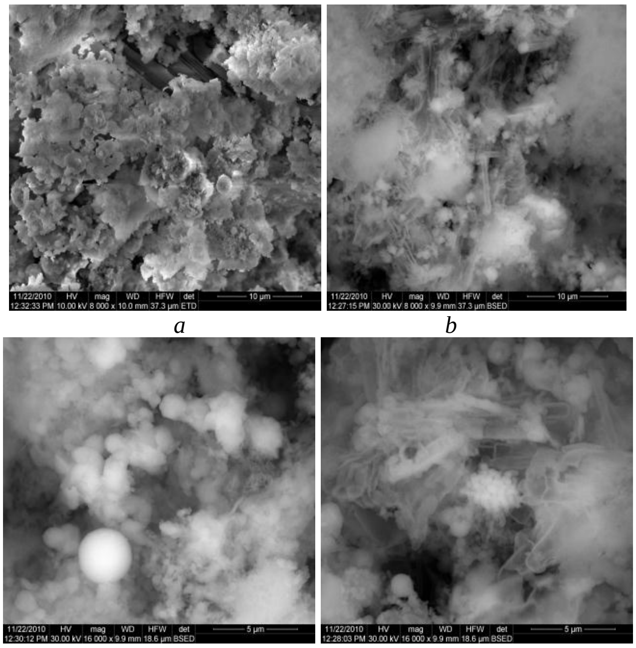


(5)

By mixing the alkaline solution (SI) and the acidic solution (SII) it was obtained a nanocomposite material, SiO_2 - PANI, which after processing, quartz filtering, washing and drying could be used as adsorbent material for aromatic amino compounds and chromium ions.

3.2. Scanning electron microscopy analysis

The SEM analysis, performed with a FEI instrument (Hitachi S4500 FESEM) revealed a morphology dominated by SiO_2 microspheres and PANI wires.



a *b*

c *d*

Fig. 2. The morphology of SiO_2-PANI microcomposite material, before (a, c) and after adsorption of aniline (b,d) at two resolutions: x8,000 (a, b) and x16,000 (c,d).

The silica microspheres and polyaniline wires change insignificantly their shape and sizes after the adsorption of aniline, Fig. 2a and 2c compared with Fig. 2b and 2d.

3.3. Energy dispersive X-ray spectroscopy analysis

Map and EDAX spectrum (Fig. 3) show the elemental distribution of the SiO_2-PANI micro-composite material, after the retention of chromium ions from phosphate solutions.

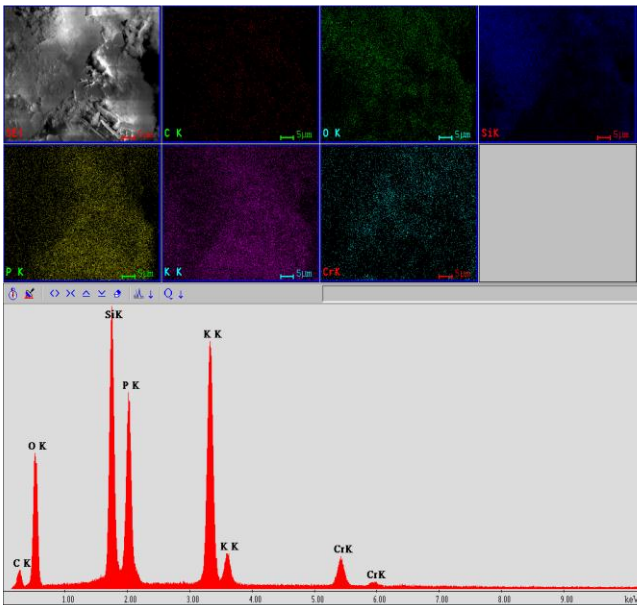


Fig. 3. EDAX image of SiO_2-PANI microcomposite material, after retenttion of chromium ions.

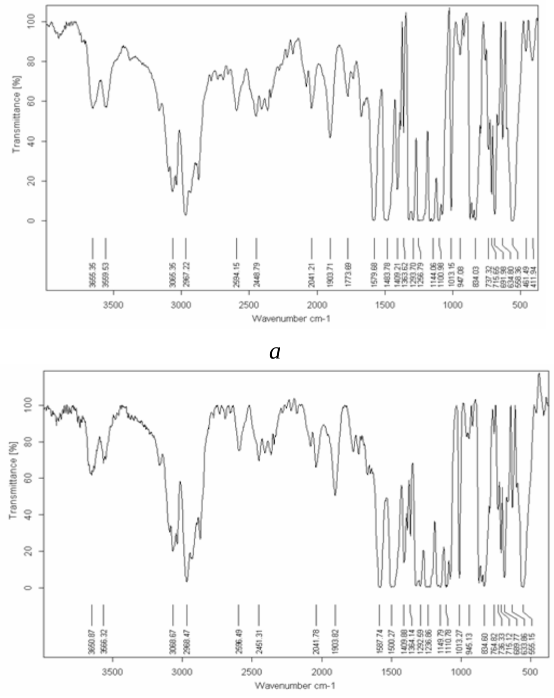
The elemental distribution shows that the micro-structured material retains chromium ions both on the silica's surface and the polyaniline's surface, combining the adsorption in silica pores with the chemical absorption onto polyaniline's surface.

3.4. Infrared spectroscopy

The FT-IR spectra were obtained by help of Bruker Tensor 27 Instrument with diamond ATR and are presented in Fig. 4 (a, b).

To characterize the materials obtained, there were analyzed by infrared spectroscopy the followings: polyaniline obtained by oxidation of aniline (filtered, washed and dried from the persulphate acidic solution), silicon dioxide - polyaniline composite obtained by mixing (ultrasonically) the alkaline solution, SI, and the acidic solution, SII, accompanied by the oxidation chemical reaction.

There were noticed interesting differences between the polyaniline spectrum (Fig. 4a) and the silica-polyaniline composite material spectrum (Fig. 4b). They suggested that the polyaniline obtained in situ interacts chemically with silicon dioxide. The spectrum region between 3000-3600 cm^{-1}, shows the formation of hydrogen bonds and the presence of electrostatic interactions which could occur most probably between the imine groups of polyaniline and the hydroxyl groups of the formed silica gel. Also, the polyaniline obtained by polymerization in the presence of potassium silicate has the specific adsorption bands shifted, thereby confirming the polyaniline-silica gel physical - chemical interaction.



a

b

Fig. 4. FTIR spectra of PANI (a) and SiO_2-PANI composite (b).

The imine nitrogen atom existing in polyaniline (emeraldine - Brönsted base) is protonated by the hydroxyl groups of the doping agent (the acidic solution of polysilicic acid), actually this process being an acid - base equilibrium. The recorded spectrum of PANI, Fig. 4a, presents a broad peak in region 3600 cm^{-1} corresponding to $–NH_2$ stretching. Also, the FTIR spectrum of polyaniline (emeraldine) shows the two characteristic absorption bands at 1293 cm^{-1} (assigned to the stretching vibration of C-N bond belonging to the secondary aromatic amine) and 834 cm^{-1} (assigned to aromatic nucleus C-H bond).

The polyaniline doping with polysilicic acid is confirmed by the presence in the FTIR spectrum of an absorption band due to the OH groups remaining non-ionized and which are present in the silica gel molecular architecture (3600 cm^{-1}).

The FTIR absorption bands at 1235 cm^{-1} and 1013 cm^{-1} are found in the doped polymer spectrum (Fig. 4b) with lower intensities, being a bit shifted as compared to the spectrum of the pure polyaniline (Fig. 4a). These absorption bands from the spectrum of synthesized material could confirm the doping of emeraldine, but also it could be an indication that there is a silica gel - polyaniline mixture. Also, the absorption band from 1149 cm^{-1} presents interest. It is found at a lower intensity in the doped polymer, being a confirmation of the chemical bond formed between the emeraldine and silica gel. It is believed that the frequency slight shift and the lower intensity of the peaks are caused by the physical-chemical interaction between PANI chains and silica gel.

3.5. Retention tests

Retention of aniline from air is an important aspect of work's toxicology both in aromatic intermediates and dyes industry, and in the synthesis of drugs and pesticides [14,15].

Although the adsorption systems with polymeric and inorganic materials present satisfactory results [16 -19], using organic-inorganic composite materials such as silicon dioxide - polyaniline (SiO_2-PANI) has the advantage of physical retention (onto the inorganic material), and a physico-chemical one onto the organic polymeric material.

The experimental results (Table 1) confirmed the excellent retention for all three types of anilines studied. Greater are the anilines' mass, better are the results recorded, for instance toluidines against anilines. For the same molecular weight the retention of the asymmetric molecules (o-toluidine) is superior to the symmetric molecules (p-toluidine).

Table 1. Anilines retention on SiO_2-PANI composite material.

	Retention %		
Feed concentration (mg/m^3)	**Anilina**	**o-toluidina**	**p-toluidina**
2	98.15	99.78	99.23
5	97.80	99.54	99.12
10	97.55	99.23	99.05
15	97.28	99.10	98.98
20	97.11	98.96	98.91
25	97.06	98.84	98.87

The adsorption isotherms confirm the qualitative judgments regarding the adsorption of the three types of aniline (Fig. 5).

The retention of chromium ions as dichromate ions from aqueous solutions of 25-200 ppm concentration is between 58% and 99% depending on the working pH (Table 2).

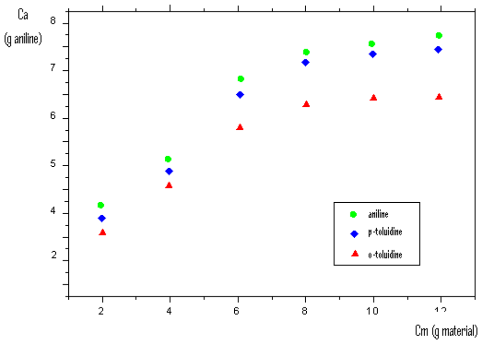


Fig. 5. Adsorption isotherms on the SiO $_2$-PANI for anilines.

The acidic pH favors the adsorption most likely due to the transition of the chromate form into dichromate form (6) and the non-protonated form of PANI into the protonated form (5).

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O \tag{6}$$

Table 2. Retention of chromium ions on SiO_2-PANI composite material.

	Retention %		
Feed concentration (ppm)	**pH=4**	**pH=6**	**pH=8**
25	99.02	88.14	75.69
50	98.96	87.53	74.34
75	98.94	86.42	71.21
100	98.89	85.77	68.90
125	98.74	84.60	62.68
150	98.25	84.21	60.44
175	97.80	84.16	59.08
200	97.76	84.08	58.05

Retention of chromium ions when the solution pass over the adsorbent material only once suggests that by carrying out a cascade adsorption in two to four steps, one can get the removal up to the accepted limit by the environmental standards in force.

The favorable influence of the pH decreasing on the retention, indicates an advanced chemical absorption of the dichromate ions onto the protonated polyaniline, the ion-ion interaction being determined.

4. Conclusions

The transformation of potassium silicate solutions resulted from the alkaline etching of silicon for electronic use (manufacture chips) into the composite silica-polyaniline, PANI-SiO_2, by mixing the polyaniline acidic solution obtained from the aniline oxidation with potassium persulphate, proved to be useful both to ultrapure silicon full recovery, and for environmental protection.

The new micro-structured material has a remarkable anilines' retention (over 98%) from gaseous effluents, but also a considerable adsorption of chromium ions (over 58%) from aqueous solutions. The anilines' retention increases with increasing molecular weight and the asymmetry of the molecules, while the adsorption of chromium ions is favored by pH decreasing.

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