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Characterization of microdevices for ferrous chloride separation for biosensing applications

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ABSTRACT

Ferrous chloride has a variety of applications such as a reducing flocculation agent in waste-water treatment, especially for wastes containing chromate, in the laboratory synthesis of iron complexes and it is employed as a reducing agent in many organic syntheses. The device used for experiment was fabricated on the silicon wafer as support for two electrodes in a SU8 polymer microchannel with an inlet, for the injection of aqueous solution of ferrous chloride, and two outlets, for the two by-products of separated solutions. The various parameters of the device were measured by White Light Interferometer (WLI) and Scanning Electron Microscopy (SEM). The magnetic field created by applying different types of potential between two electrodes determined ferrous chloride to separate in ferrous oxide and chlorine (in gaseous form). If a protein is added in this solution we have the possibility to immobilize the protein on the iron particles and on the channel area. The electrical results were collected using a semiconductor system analyzer Keithley and were examined subsequently. The Fe complexes deposited on the electrodes were characterized by XRD analyses.

1. Introduction

Ferrous chloride solution is a concentrated mineral acid solution ranging from 22–30% ferrous chloride. Ferrous chloride solution is an excellent source of Fe2+ ions where the application needs an oxidizable inorganic metal salt (in waste-water treatment). Iron is one of those types of substances that readily magnetizes. Electric currents create magnetic fields; the magnetic field produced by an electric current is always oriented perpendicular to the direction of flow. If a piece of iron is brought near a magnetic field, the electrons within the atoms in the iron orient their spins to match the magnetic field force produced by the permanent magnet, and the iron becomes "magnetized." The iron will magnetize in such a way as to incorporate the magnetic flux lines into its shape, which attracts it toward the permanent magnet, no matter which pole of the permanent magnet is offered to the iron. The important propriety of ferrous chloride is the combination between the usual behavior of a liquid and the magnetic control of its position and movement. The nanoparticles magnetized on this way can have various applications for laboratory synthesis, for metal complexes and, also, they can constitute a reduction agent in organic syntheses [1]. The use of magnetic particles for isolation and preparation of bio-cells and proteins is considered to be of great interest in bioscience [2–4]. Iron is present in nearly all living organisms. Iron-containing enzymes and proteins, often containing heme prosthetic groups, participate in many biological oxidations and in transport. Examples of proteins found in higher organisms include hemoglobin, cytochrome, and catalase [5]. In cells, iron storage is carefully regulated, "free" iron does not exist as such. To this scope, most work in this area must be done to improve the biocompatibility of materials.

In this paper we present the fabrication of a microfluidic device in order to study the separation of ferrous chloride solution in his two components and to test the immobilization of different types of protein such as Human Serum Albumin (HSA) using 3-aminopropiltrietoxisilane (APTES), dextran and alcohol polyvinyl (PVA) as immobilization agents. In order to determine the speed and dispersion of the ferrous chloride aqueous solution in the CoventorWare software has been used to simulate the microfluidic device with the ferrous chloride aqueous solution. The electrical measurements have been conducted using a KEITHLEY semiconductor analyzer. The microfluidic device have been characterized by scanning electronic microscopy (SEM) and white light interferometry (WLI).

By applying a range of voltage to the electrodes the separation of the ions in the analyzed solution takes place and, also, a diffusion process. While applying the potential, the iron nanoparticles are pushed by the electrokinetical forces to the electrodes. The concentration gradient of the iron nanoparticles determines the migration of the ions from the aqueous solution to the electrodes. By applying a positive or negative voltages on the electrodes, the iron nanopar-

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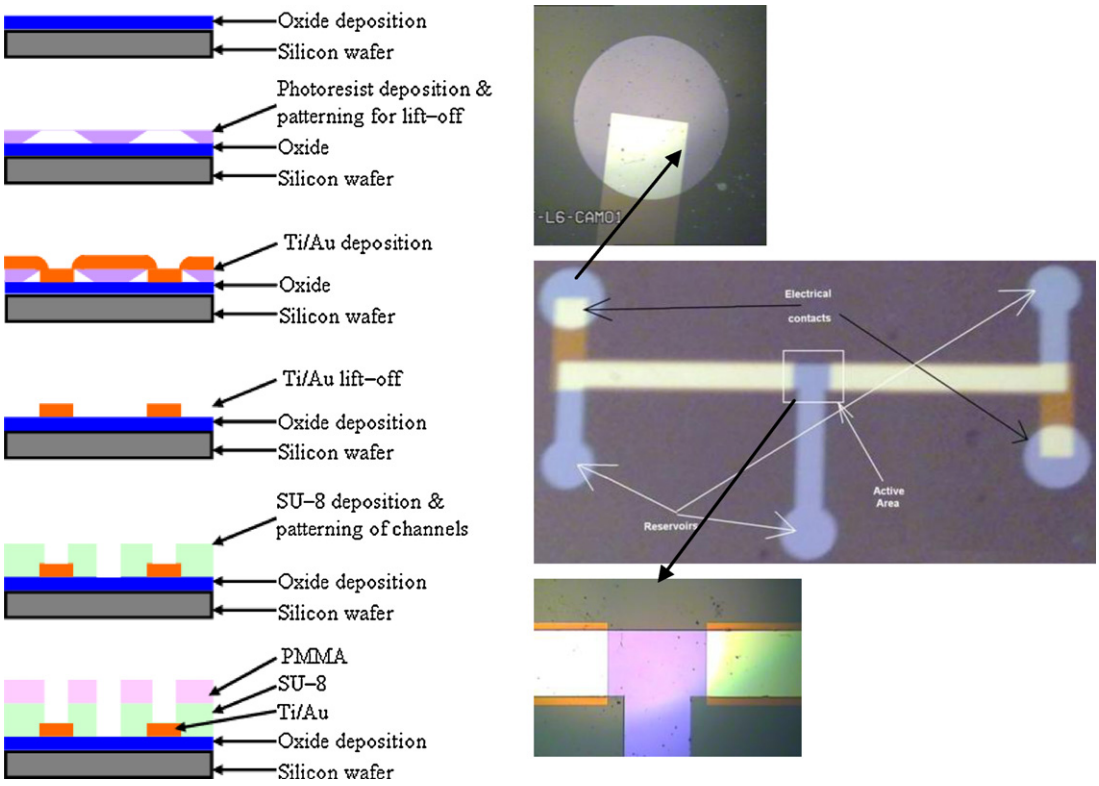

Fig. 1. Microfluidic device: (a) schematic fabrication flux; (b) optical microscope image of the fabricated device.

ticles can be both rejected and attracted to the electrodes and favors the immobilization of the proteins on the surface of ferrous chloride nanoparticles. We study the influence of the magnetic fields on the electrochemical process that occurs at the contact between an electrode and ferrous chloride solution.

2. Device and solution used

2.1. Fabrication of microchannel device

The device is fabricated on a silicon wafer with crystal orientation <1 1 1>. First, the wafer was cleaned in a piranha solution ($H_2SO_4 + H_2O_2$,) followed by a dip in ($HF + DIH_2O$) solution to remove all the native oxide and a spin dry. After this, on the Si wafer an oxide layer of 500 nm is thermally growth for isolation purpose.

"Lift-off" is a simple, easy method for patterning deposited films and films which are difficult to dry etch. A pattern is defined on a substrate using photoresist and standard photolithography. A film, usually metallic, is blanket-deposited all over the substrate, covering the photoresist and areas in which the photoresist has been cleared. During the actual lifting-off, the photoresist under the film is removed with solvent, taking the film with it, and leaving only the film which was deposited directly on the substrate. This is the method we use to pattern the electrodes. As easy it is this concept as problematic is to be realized practically because of trade off between photolithography and metallization.

So we start by treatment on hot plate at 110° C for 10 min to remove the moisture and improve the adhesion of photoresist, in plus application of HDMS (hexamethyldisilzane) will further improve the quality of photoresist adhesion. The AZ5214 photoresist is deposited by spinning to obtain a thickness of 1.5 μm. A soft bake treatment on hot plate at 90° C for 2 min to start partial evaporation of photoresist solvents and to improves etch resistance and linewidth control and to optimizes light absorbance characteristics of photoresist. The UV exposure was made using a mask contact aligner – Karl Suss MA6/BA6 (down to 1 μm resolution) and developing photoresist pattern in 3:1 AZ 400 K developer after exposure. Soluble areas of photoresist are dissolved by developer chemical. A post-develop bake is not recommended since the resist will reflow slightly.

The metal deposition of the electrodes was done by e-beam Edwards Auto500. For metallic films of non-reactive metals (Au, Pt, Pd), an adhesive film of a reactive metal such as Titanium is used. The thickness of Titanium film is 20 nm (it should be at least 20 Å for good adhesion) and the thickness of Au film is 80 nm. Prior to the metal deposition, during vacuum step, the e-beam chamber was heat it up till 180° C for 1 h and let it to cool down to promote the adhesion of metal layer to substrate. Using this process we discover that gold surface is smoother with good interface adhesion and after lift off the edges of electrodes are flat.

After metals deposition the wafer was bake on hot plate at 110° C for 10 min to will drive off excess solvent so that there will be outgassing during the treatment that will break the metal film. This operation makes easy the removal of photoresist especially when using ultrasonic agitation in acetone for 1–2 min, followed by cleaning in DI water and spin dry.

Microfluidic channel was patterned photolithography in a SU8 layer 10 μm thick. Inlet and outlet tanks have diameters of 850 μm, while the channel width is 1000 μm. The channel device has a length of 16,000 μm and width of 800 μm, but the active area of the channel is defined by area between two electrodes and channel width. These dimensions are correlated with the size of the nanoparticles contained in the sample solution, which allows them to move along the channel at electrode potential application. The schematic design and the fabricated microfluidic device is presented in Fig. 1.