Nanosieves Fabricated by Interference Lithography and Electroforming

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ABSTRACT

Self-sustaining Nickel membranes with periodic and regular distribution of pores, in the scale of hundred of nanometers, were produced by interference lithography and electroplating. The process consists in the recording of submicrometric 2D periodic photoresist columns, on a metal-coated glass substrate, using the double exposure of an interference fringe pattern. As the photoresist is a good electrical isolator, when the sample is immersed in a Ni electroplating bath, the array of photoresist columns impedes the Nickel deposition in the patterned areas. A nickel film is then growth among the photoresist columns with a thickness up to 80 % of the height of the columns. In order to release the submicrometric membrane from the substrate, a thick hexagonal Nickel sustaining structure is electroformed, using conventional photolithography. The dimensions of the sustaining structure can be adapted in order to fulfill the pressure requirements of the filtration system. The good uniformity of the pore sizes as well as the smooth of the surface make such devices very interesting for separation of particles by size in filtration systems.

Keywords: sieves, electroplating, interference lithography, photolithography, membranes

1. INTRODUCTION

The permeation of fluids through membranes is largely employed in pharmaceutical, biotechnological and food industries for removal or separation of particles and bacteria. The efficiency in the separation and retention of particles in the filtration depends on the size distribution of particles present in the solution to be filtered and on the membrane pore size distribution. Figure 1 shows a scale of sizes of the different types of particles and filtration processes.

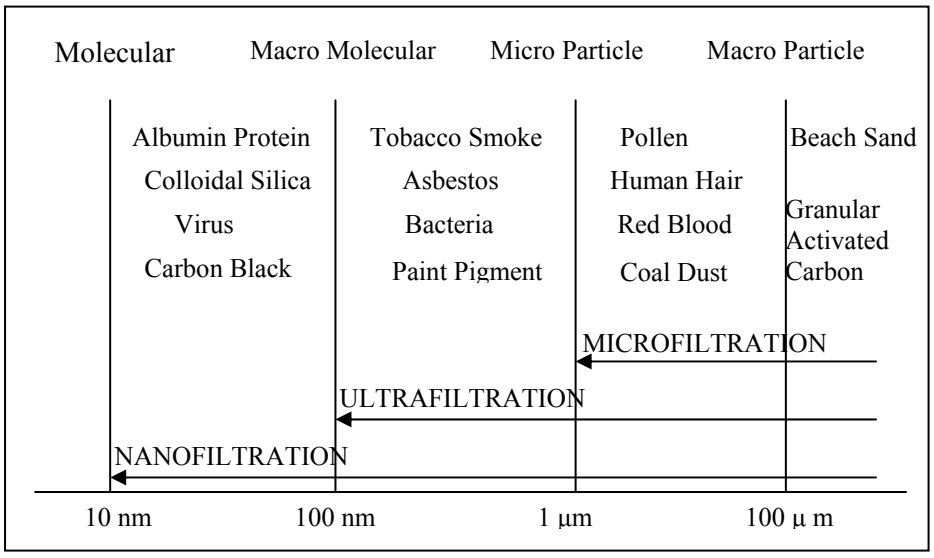

Figure 1. Scales of particles by size

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Although lived organisms can permeate through membranes with pore sizes much smaller than their self-dimensions [1], the most important parameter for controlling the selectivity in the separation or retention of particles is the pore size distribution of membranes. In applications that require the complete removal of pathogenic microorganisms the selectivity by size of the membrane is the principal mechanism that guarantee the decontamination of the permeated solution. Even the pressure employed in the filtration seems to be not important in the passage of bacteria through membranes [1].

There is a large variety of types of membranes [2] made in different materials: cellulose, polypropylene, PTFE (polytetrafluorethylene), polycarbonate, etc. Each material presents different chemical and mechanical resistance, pore density and pore size distribution. All these membranes, however, present a random network of pores with a wide distribution of pore sizes. These pore network and size distributions depend on the statistical self-assembly of material molecules during the material synthesis and of the lamination of the membrane sheets. Among the available commercial membranes, nowadays, the track-etched membranes [3] present the best quality in terms of homogeneity in the pore sizes. Even for these membranes, the pores are randomly distributed and they present a deviation of about 35 % in the pore diameter. Besides this fact, the cylindrical pores present an angle with the surface [3,4].

On the other hand, with the development of silicon technology, sieves with submicrometric dimensions have been achieved [4,5,6]. Such dimensions are comparable with those of absolute sterile membranes with the advantage that they present a regular distribution of pores with homogeneous size and shape. Besides this fact, the smoothness of the surface helps to reduce the flow resistance, increasing the velocity of filtration as well as allowing the use of retro cleaning processes. In this way, such sieves may be a promising alternative for high selectivity ultra-filtration devices.

These sieves were fabricated using the association of electron lithography, ion beam [4] or interference lithography [5,6] with silicon microelectronic technology. The sieves are formed by reactive ion etching (RIE) of a silicon nitride film coated on a silicon substrate. The membrane release is made through a strong etching of the silicon substrate, patterned from the rear side, or by engraving deep channels in the front side of the silicon substrate through the sieves [7]. The use of silicon technology, however, makes the process expensive for large-scale production and requires the construction of particular systems or devices for using the fabricated sieves

In a recent paper [8] we proposed and demonstrated the use of interference lithography associated with nickel electroforming to perform submicrometric sieves. The process is a variation of the well-known LIGA (Lithography, Galvanoformung and Abformtechnik) process [9] and can be adapted for large-scale production. The resulting sieves are free self-sustained membranes similar to those used in filtration devices. The main problem of these membranes is that due to the submicrometric dimensions of the pores, the thickness of the membranes must be also very thin, bringing difficult to their use in conventional filtration processes [8]. In the present paper we analyze the size distribution of pore of such sieves and we study the effects of the sustaining structure in order to allow their use in filtration devices.

2. ELECTROFORMING THE SUBMICROMETRIC MEMBRANE

The process used for the fabrication of submicrosieves, schematized in Figure 2, is composed of the following steps:

1) A glass substrate is coated with a thin conductive layer (of about 30nm), by sputtering, to provide the electrical contact for the electroforming.
2) A photoresist AZ 1518 (Hochst) film of about 800 nm is coated on the conductive layer by spin coating.
3) After a pre-bake for 20 minutes @ 70^{o}C, the sample is patterned using an interferometric system.
4) A thin nickel film is electroformed among the photoresist structures.

2.1. Interferometric Lithography

The interferometric lithography consists in the exposure of the photoresist film to a fringe pattern generated by the interference of two coherent beams from an Ar-ion Laser (at λ=458nm) [8]. In our setup, the periods of the fringes (Λ) can be arbitrarily chosen between 0.38 and 2 μm and the exposure area is a circular spot of about 10 cm of diameter. For this wavelength (λ=458nm) only G line types of photoresist can be used. For the AZ 1518, with 1μm of thickness, doses

of 300mJ/cm^2 are required. In our setup, using a typical laser power of 150 mW (at λ=458nm), this dose corresponds to exposure times of about 10minutes. In order to avoid fringe motion during the exposure, the holographic setup is provided with a fringe locker system [10].

The simplest way to perform two-dimensional patterns is the use of two successive exposures of a single fringe pattern by rotating the sample by 90^o between them [11,5,8]. As the rotation angle is not critical, after the first exposure the sample was rotate using as a reference the squared shape of the substrate. In this way, to pattern the sieve pores, the photoresist films were exposed twice at the same dose of 300mJ/cm^2.

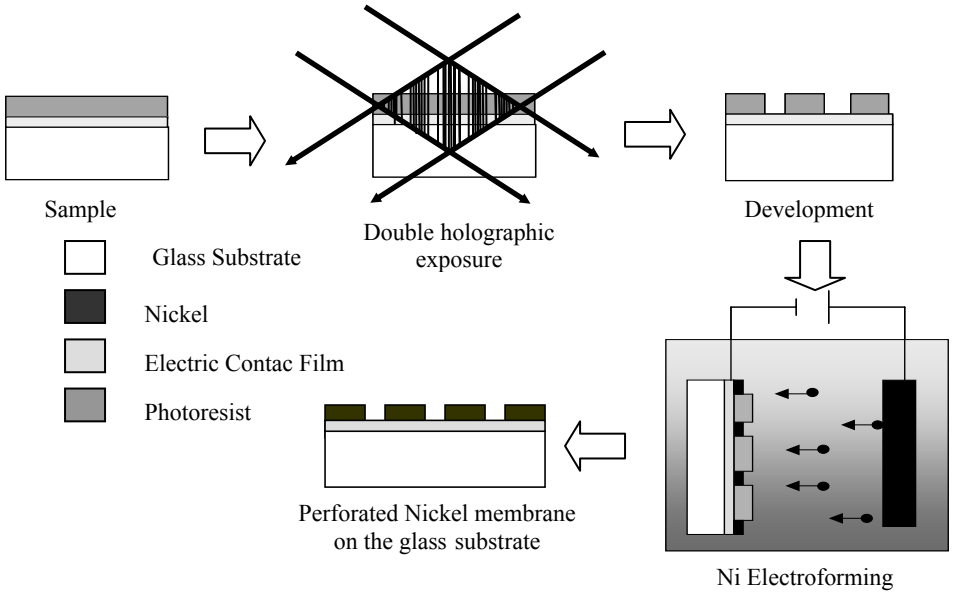

Figure 2. Scheme of electroforming the submicrometric membrane using interference lithography

After the double exposure, the development was performed by immersion in a solution of AZ developer, diluted in deionized water, during about 40 seconds. The resulting photoresist structures are columns (Figure 3) whose diameters (d) present about 20 % of the fringe period (Λ) [8]. Thus accounting to the feasible period range in our holographic setup, the diameters of the columns that we can be fabricated, are between 50nm (for the Λ= 0.38μm) and 500nm (for Λ=2 μm).

The maximum aspect ratio of such columns (h/d, with h = height and d=column diameter) depends on several parameters [12,13] such as isotropy of the development process, contrast of the interference fringe pattern, nonlinearity of the development, the absorption of the photoresist, etc. In our case we can reach aspect ratios (h/d) up to 4, as it can be seen in Figure 3.

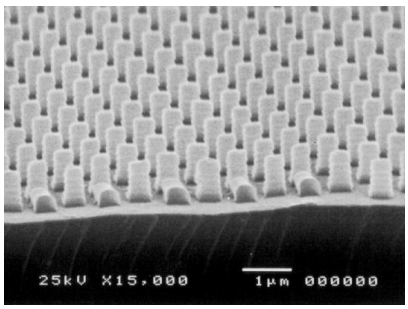

Figure 3. Typical photoresist structure recorded by double exposure by rotating the samples of 90^o between them.

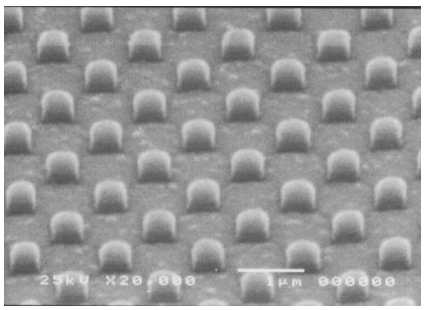

Figure 4. Nickel membrane electroformed among the photoresist structures.

2.2. The electroforming

After the rinsing and drying the samples are mounted in a cell that provide a homogeneous electric contact with the conducting layer coated on the substrate. The cell is then brought to the electrodepositing bath [9,14] to form the thin nickel sieve. The electroforming bath contain Nickel Sulphamate ($Ni(NH_2SO_3)_2$), Nickel Chloride ($NiCl_26H_20$), Boric Acid and de-ionized water. The Nickel Sulphamate ($Ni(NH_2SO_3)_2$) is the main source of Ni ions that will be deposited in the cathode while the role of the Nickel Chloride ($NiCl_26H_20$) is to promote the corrosion of the solid Ni anode, to keep unchanged the concentration of Ni ions in the bath [9,14]. The Boric Acid (H_3BO_3) avoids the changes in the pH of the bath [9,14]. If a potential is applied between the electrodes, it occurs the well-known electrolysis process ($Ni^{2+} + 2e \rightarrow Ni$) [9,14] that results in the Ni deposition on to sample.

The photoresist structures, previously recorded, act as an electric insulator thus the Ni electrodeposition occurs only among these columns where there is electric contact, as illustrated in Figure 2.

Figure 4 shows the SEM photograph of the sample with the nickel thin film deposited among the photoresist structures.

The resulting profile of the pores is the complementary profile of the photoresist structure. Thus the pore diameters will follow the column diameters. The thickness of the nickel membrane is limited up to 80 % the height of the photoresist columns otherwise the pores of nickel sieves will be closed. Considering that the maximum aspect ratio for the photoresist structures is h/d= 4, we can estimate the maximum thickness for the sieve 3.2 times the diameter of the holes (that means for pore diameters of about d = 50 nm, the maximum thickness of the sieve is 160 nm and for pore diameters of d = 500nm the maximum thickness for the sieves is 1.6μm). Thus this process results in nickel membranes of about few hundred of nanometers that cannot be self-sustained in large areas.

3. ELECTROFORMING THE SUSTAINING STRUCTURE

In order to release the thin sieve from the substrate, we developed a sustaining structure taking the advantage of the same electroforming process. The scheme of the process is schematized in Figure 5 and it is described bellow.

1) After the electroforming of the thin nickel submicrometric membrane, the sample is cleaned, dried and spin coated again with a thick photoresist AZ 4620 (from Clariant), forming films with thickness of about 4 μm;

2) After the pre-bake, the photoresist is exposed in a conventional optical lithography system, using Hg lamp. The mask, determines the geometry of the sustaining structure. In our case to maximize the useful area of the membrane we designed a hexagonal lattice mask, illustrated in Figure 6.

3) The photoresist films are developed in AZ developer diluted in deionized (DI) water for about 3 minutes, rinsed in DI water and dried in N_2 jet;

4) After development, the sample is brought again to the electroforming bath and a nickel thickness of about 4 μm is formed;

5) After the formation of the sustaining structure, the released of the membrane is made by immersion of the sample in warm acetone and then in deionized water. During the immersion in the deionized water, the membrane floats releasing the substrate. This occurs due to the low adhesion between the conductive coating and the glass substrate. By other side, the adhesion between conductive coating and the Ni is quite good allowing the release without damage the sieve. In this way, the choice of the material for the electric contact is an important process point.

The choice of the dimensions of the hexagonal structure is also an important point in the process because it determines the maximum pressure that can be applied to the membrane in the filtration device.

In our case we designed hexagonal masks (as shown in Figure 6) with different sides: 500μm, 250 μm, 15μm and 10 μm. The masks of hexagons of with 500 and 250 μm of sides were recorded in photolithes while the masks for the smaller hexagons (15 and 10μm) were recorded in chrome by e-beam. In the smaller masks the hexagons are separated by a width of L/3 (Figure 6). Although the quality of such mask were very good, the optical lithography in AZ 4620 is very difficult because the width of the bars are of the same magnitude of the photoresist film thickness (5μm), resulting in aspect ratios greater than 1.

3.1. The sustaining of the membrane

A given membrane of thickness "t", supported by holders separated from a distance "D", as shown in Figure 7, is submitted to two types of stress: "σ_t" the stress due to the tension of the membrane and "σ_b" the stress due to the curvature of the membrane. The highest stress occurs in the region membrane near to the holder where the curvature of the membrane is maximal and its value is given by [15]:

$$\sigma = \sigma_b + \sigma_t = g(\nu)\sqrt[3]{\frac{P^2 D^2 E}{t^2}} \quad (1)$$

with P the pressure on the membrane, E the Young modulus of the material and g(ν) is a function of the Poison ratio "ν" that is defined as the ratio between the lateral and axial contraction of the membrane.

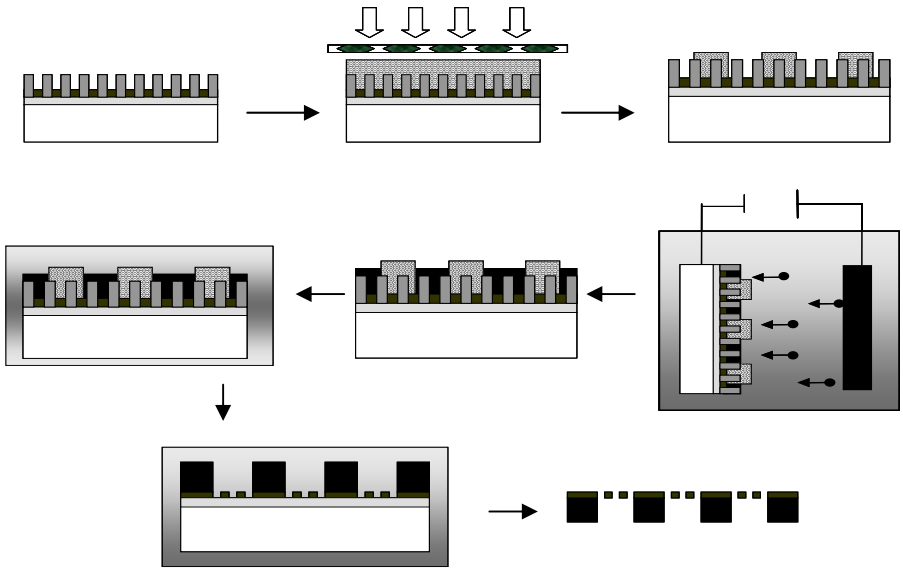

Figure 5. Scheme of electroforming the sustaining structureof using optical lithography

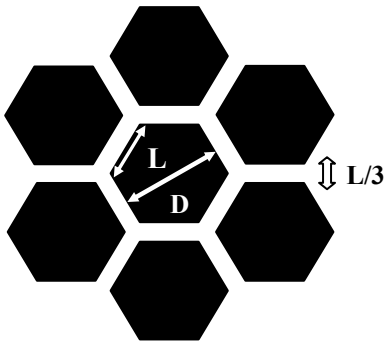

Figure 6. Hexagonal mask used to electroform the sustaining structure

For a perforated membrane the stress should be greater than that for a continuum membrane because the deflection (curvature) is greater [15].

Each membrane supports a maximum stress value σ_M. This stress value depends on the membrane parameters and on the pressure applied on the membrane P, as given by Eq. (1). Thus, for a given membrane, there is a pressure that results in this maximum stress value producing the rupture of membrane. This pressure is called rupture pressure (P_r) and is given by:

$$P_r = \frac{t}{D}\sqrt{\frac{1}{E}\left(\frac{\sigma_M}{g(\nu)}\right)^3} \quad (2)$$

In the case of a hexagonal sustaining structure each side of the hexagon (L) is related with the distance (D) (Figure 6) between the membrane holders by:

$$D = L\sqrt{3} \tag{3}$$

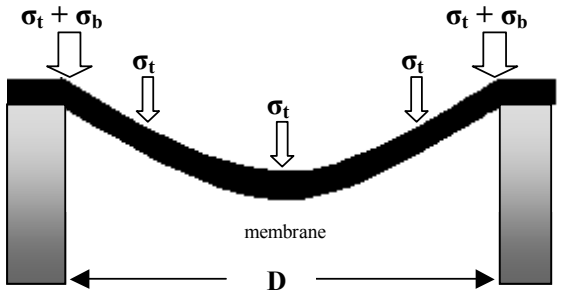

Figure 7. Scheme of the membrane holder

Thus, if the membrane thickness "t" increases the rupture pressure increases by the same proportion, as well as if sides of the hexagons (L) increases the rupture pressure decreases by the same proportion. Thus depending from the pressure used in a filtration device we can previously define the distance sides of the hexagonal structure in order support such pressure.

4. RESULTS AND DISCUSSION

Figure 8 shows a SEM (Scanning Electron Microscopy) of the submicrometric membrane superimposed with photography of the released Nickel membrane. Strong color dispersion can be observed due to the white light diffraction at the submicrometric pores as well as the presence of the hexagonal sustaining structure.

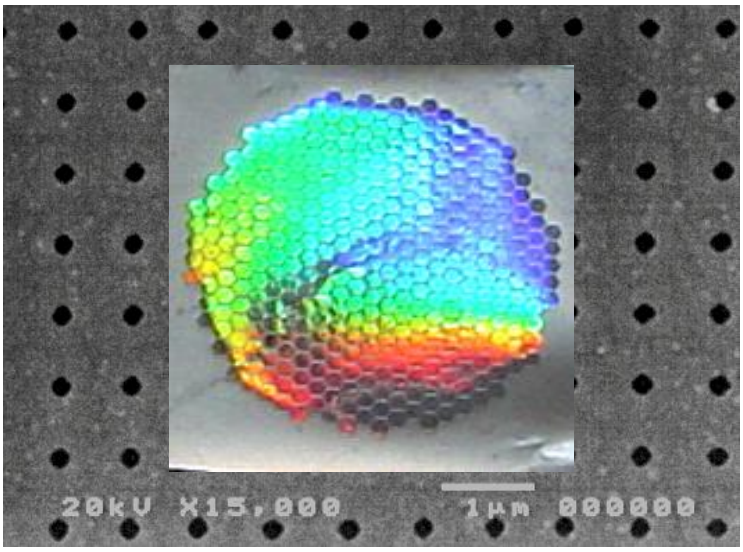

Figure 8. SEM photography of the submicrometric pores superimposed with a photograph of the membrane.

Figure 9 shows the size distribution of the pore diameters obtained from SEM photographs of different regions of the sieve. The measurement of the pore diameter was performed using the software Image Pro-Plus version 4.1 [16]. The pitch (period) of the sieve is 1 micrometer and the average diameter of the pores is 200nm. Note the very sharp size distribution of the pore sizes: the width of

the distribution at half height is about 25 nm and in the basis of the distribution of about 50 nm. This means a maximum deviation of about 10 % in the pore diameter.

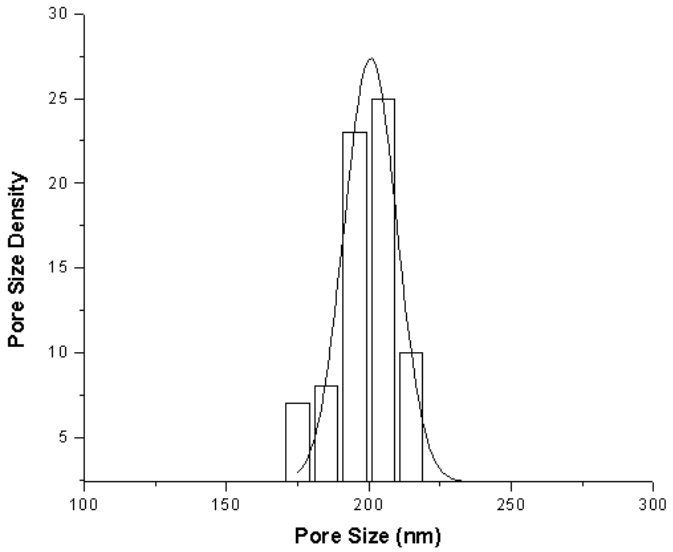

Figure 9. Size distribution of the pore diameters of the submicrometric sieve with pit of 1 μm

Experiments conducted in a cross flow type simple filtration device show that for non perforated membranes with different thickness, but with the same hexagonal sustaining structure with side of 250 μm, presented different rupture pressure as shown in Table 1. As it can be seen from this table the linear relation, given by Eq. (2), is follow.

Table 1. Rupture pressure (Pr) for membranes with different thickness and the same hexagonal sustaining structure (side of 250 μm)

P_r, Rupture Pressure (Pa)	t, Membrane Thickness (nm)	P_r/h (Pa/nm)
1515.42	300	5.05
2746.91	440	6.24
3125.83	470	6.65

Figure 10 shows an optical microscope photograph of the broken membranes with a sustaining hexagonal structure of 250μm of side. As it can be seen from this Figure, the rupture occurs in the junction between the membrane and the sustaining structure, where the stress is maximal.

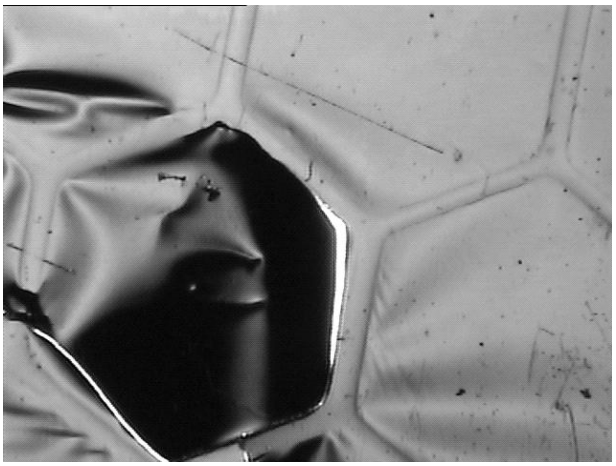

Figure 10. Optical microscope photograph of the open membrane.

5. CONCLUSIONS

We demonstrate a new process for fabrication of membranes with pore diameters in the scale of hundred of nanometers using the association of interference lithography and electroforming. The resulting membranes surfaces are smooth and the membranes are compatible with the conventional filtration membranes.

The pores size distribution is very sharp presenting a maximum deviation on the pore sizes of about 10 %. This is much better than that presented by track-etched membranes, that are the most homogeneous pore size membranes available on the market.

On the other hand, we demonstrate the importance of the sustaining structure dimensions in the applicability of the membrane in filtration devices. The rupture pressure of the membrane is directly proportional to the membrane thickness and inversely proportional to the lateral size dimensions of the hexagons. From our preliminary results (Table 1) if we use hexagons with sides of about 25μm pressures of about 30,000 Pa can be reached in our membranes.

Acknowledgments

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