INVESTIGACIÓN REVISTA MEXICANA DE FÍSICA **50** (5) 515–517 OCTUBRE 2004

Micro-structures made with a capillary

T. Lopez-Rios, F. Gay, R.A. Vazquez-Nava*, and A. Barbara
Laboratoire d'Etude des Propriétés Electroniques des Solides, CNRS,
B.P.166, 38042 Grenoble Cedex 9, France

S. Pairis
Laboratoire de Cristallographie, CNRS,
B.P.166, 38042 Grenoble Cedex 9, France

Recibido el 19 de enero de 2004; aceptado el 19 de marzo de 2004

A method to elaborate micro-structures of ionic crystals based on the deposition of drops on a surface with a capillary is presented. The typical dimension of these structures is in the micron range. The possible applications of such structures in optics are discussed.

Keywords: Drops deposition; microstructures; crystal growth; photonic crystals.

Presentamos un método para elaborar microestructuras de cristales iónicos que se basa en la deposición de gotas en una superficie usando un capilar. El tamaño típico de estas estructuras es del orden de micras. Se discute las posibles aplicaciones de estas estructuras en óptica.

Descriptores: Deposición de gotas; microestructuras; crecimiento de cristales; cristales fotónicos.

PACS: 81.15.-z; 81.10.-h; 81.16.-c

1. Introduction

In the last years, a fantastic progress has been made on the elaboration of nano-structures. To a large extent this progress was driven by the micro-electronic needs to make circuits at such scales. Ion or electron beam lithography are standard methods to engrave electronic circuits. An overwhelming amount of academic work on electronic transport and magnetism has been benefited with this technology used to structure silicon or silicon oxide surfaces. Relevant phenomena usually occur for samples structured at the scale of the wavelength of light, but in some cases features with much smaller dimensions give rise to interesting effects [1]. The main shortcoming of this technology is to be poorly adapted to some materials like complex oxides or ionic crystals. On this communication, we will describe a method to create an ordered array of ionic micro-crystals. Ionic crystals have noticeable optical features in the infrared, between the frequencies of transverse ω_T and longitudinal ω_L optical phonons, that for most of the materials correspond to wavelengths between 10 and 30 microns. For frequencies in between ω_T and ω_L, the dielectric constant is negative and the ionic crystals have surface phonon resonances. Corrugated ionic crystal present interesting phenomena on this spectral range. For instance, in case where diffracted orders and surface optical phonons occur at the same wavelength, a resonance may exist similar to x-ray anomalous diffraction. In this paper, in Sec. 2 we will briefly discuss some methods to draw microscopic objects with a tip, in Sec. 3 we shortly enumerate the methods to generate drops, and their applications and in Sec. 4 we will present the method we have used to deposit drops with a capillary.

2. Drawing with tips

It is well known that on human history men first engraved stones and later on, 30 thousands years ago, improved their art and painted by depositing clay and pigments leaving us beautiful cave paintings. Some one has said that as in the human arts, the leading edge on technological engraving has been made depositing matter rather than taking matter away. Today, it is possible to draw at atomic scales moving atoms on cold surfaces with a scanning tunneling microscope(STM) [2]. Very small dots can be made depositing metal atoms from the STM tips by electric pulses [3], or by laser ablation [4]. Chemical reactions induced by polarized AFM tips permit anodization of silicon in a controlled manner with a finesse of only few nanometers only [5]. Local chemical reactions can be made with a capillary in contact with a surface [6]. Near field optical microscopy allows to encode photoresist with a lateral resolution better than with a micron [7]. Finally, with the commonly named dip-pen technology, an AFM tip previously dipped into a solution with polymers, transfers to the surface the polymers in a very similar way that the ink is deposited on a paper with a fountain-pen [8]. To the best of our knowledge this technology has been employed till now with polymers only. The method presented here uses a capillary to transfer a liquid drop to a surface. This principle, lying in some extent in between the dip-pen method and the ink-jet deposition, has recently been employed to deposit photoresist [9] and is discussed in the next paragraph.

3. Drawing with drops

Since long ago, drops and aerosol generation are topics of great importance in chemistry, biology and material science(painting, enhanced reactivity of chemical reactions, etc). Aerosol CVD is a standard method to elaborate many complex inorganic materials. This method is based on the simultaneous generation of drops containing different radicals which react drop to drop with a good stoechiometry. This technology is also based on the simultaneous generation of a large amount of drops. A further step forward was made more recently with the development of ink-jet technology to control individual drop deposition. This technology, which has a tremendous economical impact, is being used to print digital images and many other applications like prototyping, deposition of biological materials, fabrication of micro-optics elements, and to make metal tracks on electronic circuits. Ink-jet printing is based on the drop deposition on a given surface with the subsequent evaporation of the solvent. Roughly speaking we can classify ink-jet devices of three types: those using charged drops controlled by polarized plates, those using piezoelectric forces to exhaust the drop through a nozzle, and those using a heater element to spit the drop by boiling pressure. In all cases, the main limitation is the drop size which is larger than ten microns.

4. Drawing with drops deposited with a capillary

It is known that when a surface is in contact with a capillary containing a liquid which wets the surface, a meniscus is formed between the surface and the capillary. In our experiments, drops are deposited on the surface in two steps: in the first one, a meniscus is formed by contact of the capillary with the surface, while in the second one, the drop is subsequently deposited by pulling out the capillary from the surface. To do so in a controlled manner, the sample is placed on a X-Y micro translation stage (M111) furnished by a PI Physik Instrumente which allows to place and move the sample with an accuracy of more than 7 nm, using computing control. The capillary vertical displacement to make contact with the surface is provided by a piezo (P-810.30 from PI Physik) which acts to deposit drops at desired positions. The lateral dimensions of the drops are basically given by the capillary diameter. Capillaries are made by drawing a glass tube locally heated by a filament. We used a home made puller similar to those currently used by biologists to work with cells. The inner diameter of the capillaries we have used is about 20 micrometers.

We have realized that it is convenient that the narrow part of the capillary extends over several millimeters in order to have some elasticity to avoid a break down when the capillary touches the surface. The capillary contact is observed with a video camera and a microscope oriented in a direction almost perpendicular to the capillary. The samples presented here are made of $CuSO_4 \bullet 5H_2O$ which is the natural structure of copper sulfate. The deposition of $CuSO_4$ is made after the rapid evaporation of the water in the drop. It is remarkable that the final deposit is almost independent of the $CuSO_4$ concentration. This is probably due to the fact that the continuous evaporation of water at the capillary end leads to a higher concentration almost independent of the concentration in the capillary. Figure 1 shows $CuSO_4$ bumps on a silicon surface coated with natural oxide.

A noticeable effect occurring with small drops is the formation of crystalline domes rather than crystallites randomly oriented. The explanation is the following: the ions concentration is originally homogeneous in the drops, but immediately after the drop deposition, the surface evaporation increases the ion concentration in the surface region. The ion transport does not compensate concentration changes due to water evaporation at the surface. This unbalanced process leads to a saturated solution at the neighborhood surface and a subsequent crystallization at the surface. The crystal shape is imposed by the drop surface rather than by the usual atoms displacement occurring during the crystal growth. This is an interesting phenomenon which deserves further investiga-

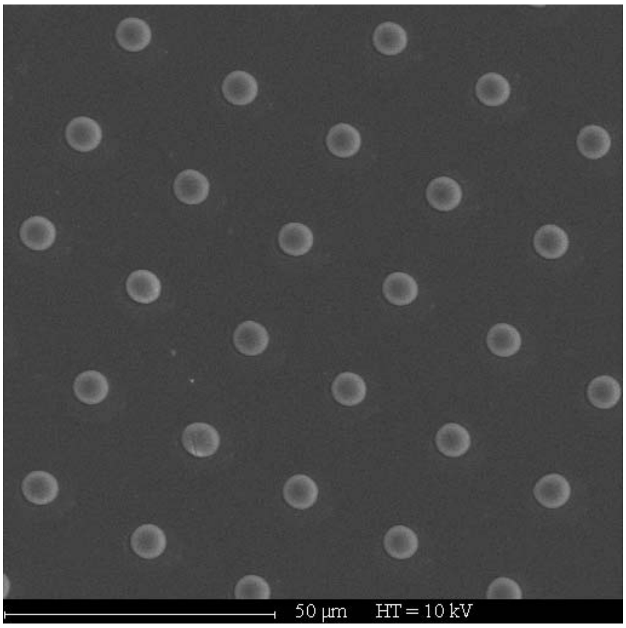

FIGURE 1. $CuSO_4$ domes on silicon surface naturally oxidized.

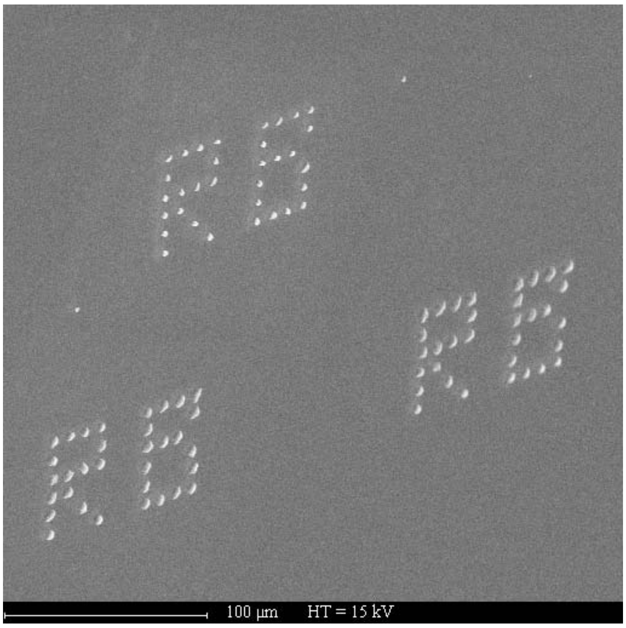

FIGURE 2. R and B letters plotted with a $CuSO_4$ solution into the capillary.

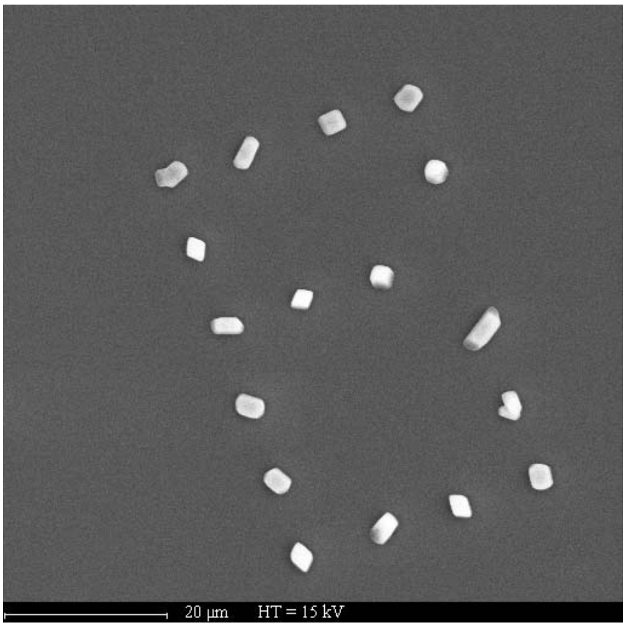

FIGURE 3. $CuSO_4$ crystallites formed after recrystallization of the original domes.

tions. Our experimental set-up allows to choose arbitrarily the position where the drop will be deposited. In Fig. 2, several R B letters made with $CuSO_4$ are shown. An other effect, some times observed, depending on the ambient humidity, is the dissolution of the crystal domes by the naturally absorbed water and a subsequent recrystallization. As this process is very slow (several hours to some days), now the crystals have the usual crystal shape and are randomly oriented as shows Fig. 3. The method is rather general and can be employed with a large number of fluids including those of biological interest, provided that the liquid wets the surface to some extent. Concerning optics, polymers, and metal colloids are good candiadates to make refractive and diffractives structures. Devices like micro-lenses arrays, wave guides, and Fresnel lenses may be fabricated depositing drops on transparent substrates.

5. Conclusion

To conclude, we will mention that several other compounds can be deposited by this method. Preliminary studies are in progress concerning conducting polymers and metallic nanoparticles which can, as in the case of salts, be deposited with the drops. This method seems to us to be well adapted to generate photonic structures. We plan to measure, quite soon, the infrared reflectivity of samples as those shown in Fig. 1. We are confident that resonant phenomenon can be observed, and can be understood with a dipolar representation of matter.

Acknowledgments

We are indebted to Jacques Marcus for help and advices. We thank Peter Apell, Alain Baronnet, Etienne Gheeraert, Pascal Quémerais, and Jean-Louis Tholence for their useful discussions. One of us (RAVN) thanks the Université Joseph Fourier (Grenoble) and the french "Ministère de la Recherche" for financial support. This work was presented in the Symposium in honor to Professor Ruben G. Barrera in his 60th birthday. The Symposium was held on the 3rd and 4th of April of 2003, at the Instituto de Física, UNAM.

∗ Centro de Investigaciones en Óptica, Loma del Bosque 115, Lomas del Campestre León, Gto 37150 México.

1. A. Barbara, P. Quémerais, E. Bustarret, and T. Lopez-Rios, *Phys. Rev. B* **66** (2002) 161403(R).
2. D.M. Eigler and E.K. Schweizer, *Nature* **344** (1990) 524.
3. H.J. Mamin, P.H. Guethner, and D. Rugar, *Phys. Rev. Lett.* **65** (1990) 2418.
4. J. Jersch and K. Dickmann, *Appl. Phys. Lett.* **68** (1996) 868.
5. P. Avouris, T. Hertel, and R. Martel, *Appl. Phys. Lett.* **71** (1997) 285.
6. A. Lewis *et al.*, *Appl. Phys. Lett.* **75** (1999) 2689.
7. F. H'Dhili, R. Bachelot, G. Lerondel, D. Barchiesi, and P. Royer, *Appl. Phys. Lett* **79** (2001) 4019.
8. R.D. Piner, Jin Zhu, Feng Xu, Senghun Hong, and C.A. Mirkin, *Science* **283** (1999) 661.
9. Mun-Heon Hong, Ki Hyun Kim, Joonho Bae, and Wonho Jhe, *Appl. Phys. Lett.* **77** (2000) 2604.