Vol. **105** (2004) *ACTA PHYSICA POLONICA A* No. 3

Fabrication and Characterization of Semiconductor CuCl Nanocrystals

S. Mahtout, M.A. Belkhir* and M. Samah

Solid physics group, University of Bejaia, 06000 Bejaia, Algeria

(Received August 7, 2003)

CuCl nanocrystals were elaborated in a NaCl ionic matrix by doping the latter with copper powder during growth. Optical absorption measurements revealed nanocrystals with a mean size of order 32 Å. This is consolidated by the Raman scattering measurements which showed nanodomains of similar size. X-ray diffraction measurements indicate a good crystallinity of the matrix and confirm the presence of CuCl nanocrystals within our samples. The annealing effect at 300°C showed an increase in CuCl nanocrystal size with annealing time and demonstrated clearly the existence of a compound containing copper within our samples.

PACS numbers: 78.67.–n, 78.40.Fy, 78.40.–q

1. Introduction

Since the discovery of the transistor, there is more than fifty years, the semiconductors play a major role in electronics, and consequently in our everyday life. At the end of the seventies, with the introduction of new techniques of controlled crystal growth, such as metal-organic chemical vapour deposition or molecular beam epitaxy, etc., growth of solids of low dimensionality (two, one, or even zero) became possible. This type of materials is very attractive both for applications and theoretical investigations. Indeed, we may use them to fabricate lasers [1], optical amplifiers, or solar cells. In the field of electronics, the growing number of taken patents [2, 3] allows to suppose that the applications of nanocrystals will be very important in the near future. The work presented here consists in working out of CuCl nanocrystals in a NaCl ionic matrix and their characterization. Optical absorption measurements at ambient temperature are followed by a study

---

[*] corresponding author; e-mail: belkhir_a@yahoo.fr

of the effect of thermal annealing on the optical absorption spectra. Then X-ray diffraction (XRD), photoluminescence, and Raman diffusion measurement are also studied.

2. Experiment

Our samples were fabricated using the Czochralski technique. The principle of the method consists in melting the material, which is to be crystallized, in a melting pot. Crystallization is then obtained due to a weak temperature gradient. The latter is settled by the formation of a meniscus around a seed crystal in contact with the melt surface. Doping of the melted NaCl was done at temperature averaging 900°C. Chosen pulling parameters are one centimetre per hour and one turn per minute, respectively, for translation and rotation movements. One finally obtains pastilles in the form of discs with about 1 mm of thickness and 1 cm of diameter. These pastilles were then subjected to various methods of characterization.

3. Results and discussion

Optical absorption measurements of NaCl doped with copper were made on several samples. Figure 1 shows an example of the obtained spectra. The latter presents several peaks in the visible and near ultraviolet. The peaks appear as a shouldering [4] (addition of peaks originated from different sizes). In the ideal case where the nanocrystals have all the same size, the peak should be very fine. The broadening of the peak tells us about the importance of the size dispersion of the nanocrystals [5]. The first observed peak is located at the neighbourhoods of 255 nm. This one is allotted to the internal transitions from Cu^+ monomeric [6, 7]. Another peak appears in the neighbourhoods of 340 nm. At this stage, the nature

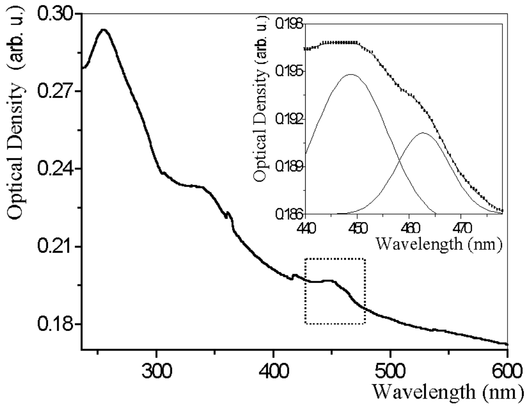

Fig. 1. Optical absorption spectrum of NaCl doped by copper.

of this peak is not known [8], but the effect of thermal annealing at 300°C shows a behaviour of a compound containing copper, as will be seen further. The very fine peaks which appear at 307, 360, and 417 nm in the spectrum are due to the change of the lamp of the measuring equipment. This change occurs automatically to sweep all the frequencies of the range of measurement. In the visible part of the absorption spectrum, one can see the existence of two peaks towards 435 nm and 469 nm shown in top of Fig. 1. According to Dijken et al. [9], these transitions are due to trap levels located in the forbidden band of CuCl nanocrystals. Figure 2 shows the part of Fig. 1 magnified in the region 368–378 nm. Fitting with four Gaussian functions, we obtain four lines located at positions: 368, 371, 373, and 375.5 nm. The first and the fourth are allotted to $Z_{1,2}$ and Z_3 excitons, respectively, with a spin-orbital splitting of 66 meV. This value is sensibly equal to that of 69 meV given by Cardona [10] and Goldmann et al. [11]. The energy position of these excitons is shifted to the high energies compared to that of excitons in bulk crystal [10, 12]. This is due to the quantum confinement effect. To estimate the size of nanocrystals, we used the formula of weak confinement given by Ekimov et al. [13, 14]:

$$E = E_{\mathrm{g}} - E_{\mathrm{exc}} + \frac{\hbar^2 \pi^2}{2Ma^2}, \tag{3.1}$$

where E is the position of the excitonic line, E_{g} — the gap of the considered material, E_{exc} — the binding energy of the exciton, $\hbar$ — the Planck constant, M — the total mass of the electron–hole quasiparticle, and a — the nanocrystal radius assumed of spherical form. For CuCl, we have $M = 2.5m_0$, $E_{\mathrm{exc}} = 152$ meV [15]. Knowing that the peak with 373.5 nm of Fig. 2 corresponds to that of Z_3 exciton, one finds a diameter $2a = 32$ Å.

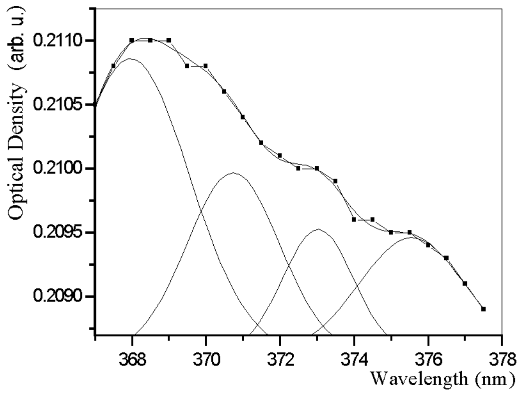

Fig. 2. Optical absorption spectrum of CuCl nanocrystals.

On the basis of the fact that energy bands, similar to those of excitons in bulk CuCl, are observed in the transparent area of the absorption spectrum of

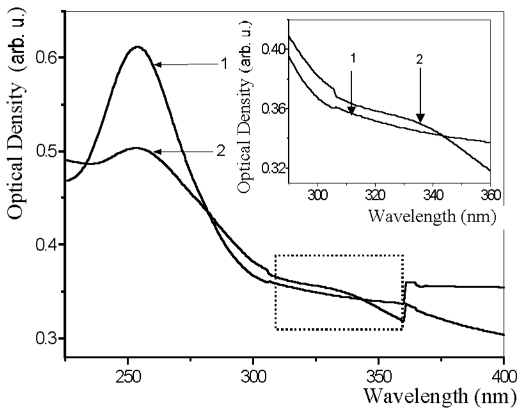

Fig. 3. Evolution of the optical absorption spectrum according to the annealing time at 300°C: (1) rough sample, (2) after 24 hours of annealing.

NaCl, it is allowed to suppose the existence of nanocrystals of CuCl in a NaCl matrix strongly doped by copper. The origin of these bands is explained by the formation of nanocrystals of CuCl in the NaCl matrix by fixation of the Cu^+ ions. In this part, we will study experimentally the behaviour of the optical absorption spectra of the NaCl samples doped by copper, according to the annealing time at 300°C. Optical absorption measurements are taken after each stage of annealing. The results are presented in Fig. 3 for rough sample (curve 1) and after 24 hours of annealing (curve 2). The remaining results are given in Table. During the various stages of annealing, we note, according to time, a progressive reduction of the line corresponding to the Cu^+ ions (to 255 nm) and a simultaneous and progressive appearance of the line at 340 nm as shown in the top of Fig. 3. It is on the basis of this particular behaviour that we allot this peak to a compound containing copper (CCC). This result can be explained by the fact that because of annealing at 300°C, the aggregates of copper ions, inside the sample, are dispersed in the form of separated ions and their interaction with the matrix and with the

TABLE

Evolution according to time of the CCC peak with respect to the Cu peak at 300°C.

Time [h]	Peak Cu [arb.u.]	Peak CCC/Peak Cu
0	0.6124	0.5452
8	0.5884	0.5781
12	0.5724	0.6163
16	0.5469	0.6328
24	0.5039	0.6945

other elements which might exist as impurities gives rise to aggregates of this material. The increase in the peak corresponding to the CCC can be explained by the increase in the number of aggregates of this material. The optical absorption spectrum of CuCl nanocrystals, after 24 hours of annealing is shown in Fig. 4. We observe a displacement of the Z_3 peak position of 375 nm at 379 nm (towards weak energies). The shift of the Z_3 exciton peak toward the long wavelength side is attributed to the increase in the size of CuCl nanocrystals with annealing time. This displacement induces an increase in the CuCl nanocrystal size of 32 Å to 50 Å. This behaviour is explained by the quantum confinement effect; when the size increases, the quantum confinement effect decreases and the energetic position of CuCl excitons passes towards weak energies.

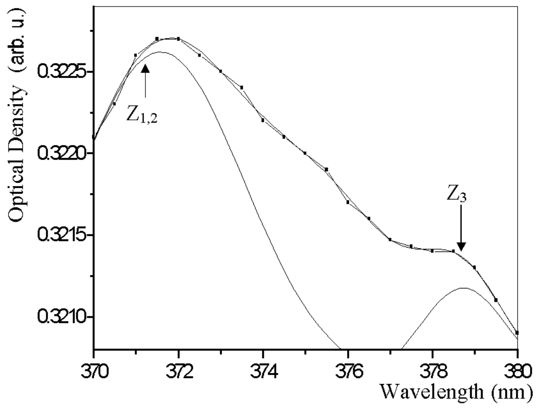

Fig. 4. Optical absorption spectrum of CuCl nanocrystals after 24 hours of annealing at 300°C.

XRD measurements were taken on several samples and the obtained spectra are all identical. Let us note that, by using a monochromator, only the line K_α of copper was selected from the source of X-rays. The spectrum of Fig. 5 presents an example of these results. This one consists of two principal lines with the positions $2\theta = 31.68°$ and $2\theta = 66.24°$. The first corresponds to the diffraction from the plane (200) of NaCl and the second to its harmonic (400). This rises from the comparison of the spectra obtained according to ASTM card (American Society for Testing and Materials) of NaCl. The appearance of these two harmonics confirms well the good monocrystallinity of the fabricated matrix. The other lines, of low intensity compared to those of the matrix, appear at $2\theta = 28.39°$, $2\theta = 33.32°$, $2\theta = 47.52°$, $2\theta = 56.32°$, $2\theta = 69.44°$, and $2\theta = 76.68°$. The latter correspond, according to ASTM cards, to the plane (111), (200), (220), (311), (400), and (331), respectively, of a CuCl crystal of zinc blende structure with a cell parameter of 5.416 Å. This result confirms the presence of CuCl nanocrystals in the matrix.

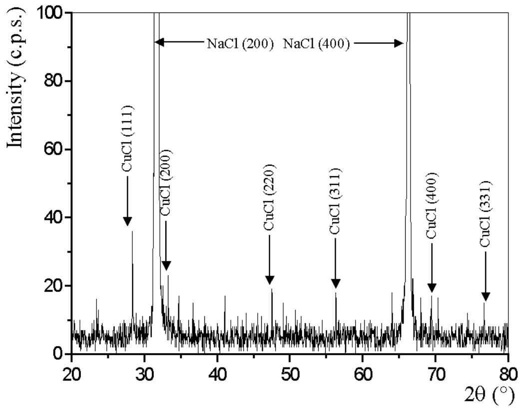

Fig. 5. XRD spectrum of NaCl sample doped by copper.

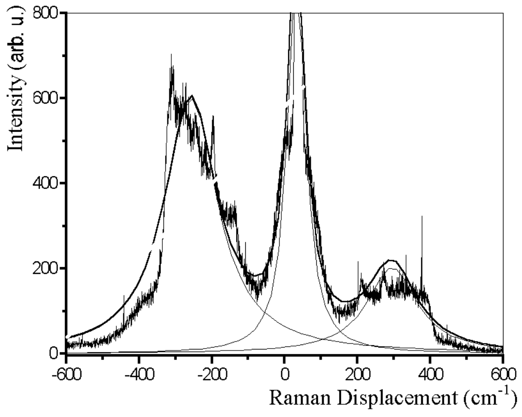

Fig. 6. Raman diffusion spectrum of NaCl sample doped by copper.

The results of measurement of the Raman diffusion on the NaCl sample doped by copper are presented in Fig. 6. The Raman diffusion low frequency can reveal the presence of nano-heterogeneities inside our samples [16, 17]. The presence of the band at very low frequency 37 cm^{-1} was connected with the inelastic scattering of the light by the natural vibrations of nanodomains in the NaCl matrix. As one can see it on the same figure, we have in addition a Stokes band at -280 cm^{-1} and an anti-Stokes band at $+280$ cm^{-1} in relation to these nanodomains.

The size of these nano-heterogeneities is estimated by the formula of Duval et al. [16]:

$$2a = \frac{sv}{c\omega}, \tag{3.2}$$

where v is the sound velocity in the nanodomain, c — the celerity of the light in the vacuum, $2a$ — the diameter of the particle, ω — the position of the Raman band low frequency, and s — the form factor which varies approximately between 0.5 and 0.8 according to the shape of the nanodomain. In our case where the sound velocity is on average equal to approximately 5300 m/s and where the band position is $\omega = 37$ cm^{-1}, one finds a nanodomain average size of $2a = 31$ Å. In good agreement with the value of the average size estimated by the optical absorption measurements, this result confirms well that this nanodomain represents the CuCl nanocrystals.

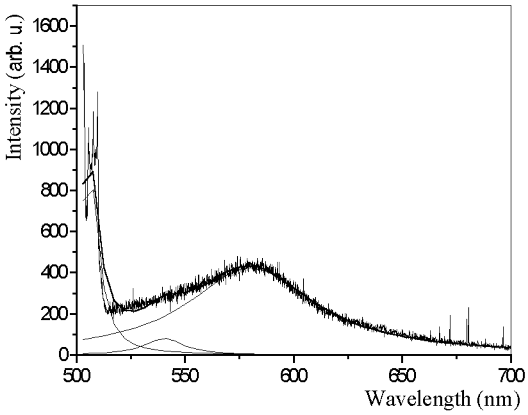

Fig. 7. Photoluminescence spectrum of NaCl sample doped by copper.

Measurements of photoluminescence were taken at the ambient temperature with an excitation of 488 nm which appears in the obtained spectrum (Fig. 7) at the same position. This spectrum shows a very apparent peak at 576 nm very broadened on the side of low wavelengths. The deconvolution of the curve by two Gaussians shows the existence of two peaks at 539 nm and 579.5 nm. These are allotted to the emission of defect such as the F-centre in the samples [18], explaining the greenish-yellow colour of the samples. Indeed, the wavelength 539 nm corresponds to the green and 579.5 nm to the yellow. The peaks corresponding to CuCl are not observed, since the energy of the radiation used (2.54 eV) is not sufficient to excite the levels of $Z_{1,2}$ and Z_3 excitons which are located between 3.2 eV and 3.4 eV (387.5 and 364.5 nm).

4. Conclusion

In this work we succeeded to fabricate the CuCl nanocrystals by doping the NaCl matrix during growth by a fine powder of copper. The size of CuCl nanocrystals is estimated to be 32 Å. The displacement of the excitonic peak position of CuCl towards high energies is due to the quantum confinement effect.

XRD and Raman scattering measurements confirmed well the formation of CuCl nanocrystals of zinc blende structure and a cell parameter of 5.14 Å. The study of the thermal annealing effect at 300°C showed an increase in the size of CuCl nanocrystals with annealing time and shows that the peak which appears in optical absorption measurements at 340 nm belongs to a compound containing copper.

References

[1] R.W. Siegel, E.Hu, D.M. Kox, H. Goronkin, L. Jelinski, C.C. Koch, J. Mendel, R.C. Roco, D.T. Chaw, WTEC US Pannel Rapport International Technology Research Institut, 1999.

[2] P. Alivisatos, V. Colvin, U.S. Patent 5 018, 751, 1989.

[3] M. Bawendi, K. Jensen, B. Daboussi, J. Rodrigguez-Viego, F.V. Mikulec, U.S. Patent 6, 207, 2001.

[4] M.A. Chamarro, V. Voliotis, R. Grousson, P. Lavallard, T. Gacoin, G. Counio, J.P. Boilot, R. Cases, *J. Cryst. Growth* **159,** 853 (1996).

[5] O. Lublinskaya, S. Gurevich, A. Ekimov, I. Kudryavtsev, A. Osinskii, M. Gandais, Y. Wang, *J. Cryst. Growth* **158,** 203 (1995).

[6] H. Kishishita, *Phys. Status Solidi B* **55,** 399 (1973).

[7] S. Nagasaka, M. Ikezawa, M. Veta, *J. Phys. Soc. Japan* **20,** 1450 (1995).

[8] T. Itoh, *Phys. Status Solidi B* **145,** 567 (1988).

[9] A. Van Dijken, E.A. Meulenkamp, D. Vanmaekelbergh, A. Meijerink, *J. Lumin.* **90,** 123 (2000).

[10] M. Cardona, *Phys. Rev.* **129,** 69 (1963).

[11] A. Goldmann, J. Tejeda, N.J. Shevchik, M. Cardona, *Solid State Commun.* **15,** 1093 (1974).

[12] S. Park, I. Kim, K. Jang, S. Kim, C.D. Kim, Y. Yee, G. Jeen, *J. Phys. Soc. Jpn.* **70,** 3723 (2001).

[13] A.I. Ekimov, Al.L. Efros, A.A. Onushchenko, *Solid State Commun.* **56,** 921 (1985).

[14] A.I. Ekimov, A.A. Onushchenko, A.G. Plyukhin, Al.L. Efros, *Sov. Phys.-JETP* **61,** 891 (1985).

[15] P. Gilliot, Ph.D. thesis, Université de Strasbourg, France, 1990.

[16] E. Duval, A. Boukenter, B. Champagnon, *Phys. Rev. Lett.* **56,** 2052 (1986).

[17] M. Philippe, *Phys. Rev. Lett. B* **77,** 557 (1997).

[18] C. Kittel, *Solid State Physics*, 5th ed., Dunod, Paris 1983 (in French).