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Magnetoresistance Transition on Nano scale Bismuth

A. Bahari[1], F. Asrafi[2], A. Babanejad[2] and A. Hajazi[2]

[1]Department of Physics, University of Mazandaran, Babolsar, Iran
[2]Department of Science, Payam E Noor University, Sar, Iran

ABSTRACT

Recently, interest in magnetotransport in bismuth is renewed because of the observation of the metallic temperature-dependence of the in-plane resistivity into an insulating-like one when a magnetic field of a few tens of mTesla is applied perpendicular to the sample plane. This procedure makes bismuth a promising candidate for applications, such as magnetic field sensors. To make high quality bismuth nano particles, it is necessary to make the grain sizes large as synthesised with sol – gel method at different contents which can be a judicious combination of lattice-matched substrates for growing bismuth nano particles with large grains. Magnetoresistance in bismuth films is also limited by grain boundary scattering. We have demonstrated a series of experiments to synthesise bismuth nano particles by sol - gel method which yield bismuth films with very small magnetoresistance. These films may even behave in a non-metallic manner with the resistance increasing with shrinking the bismuth grain size down to 50 nm.

Keywords: Nanostructures, Bismuth, Magnetotransport and sol-gel method.

INTRODUCTION

Semimetal bismuth has been interest of study for many years, because of it many special properties and its very low carrier density (~10^{23} m^{-3}) and low Fermi energy (~25meV). Bismuth provides great convenience in studying the quantum size effect in many aspects. Nano scale bismuth structuress, with their thicknesses comparable to the electron wave length (~ 300 Å), have been of great interest in the study of the quantum size effect, semimetal-semiconductor transition and magnetotransport. Some researchers [1-5] have studied the magnetotransport of the bismuth nano particles and reported that oscillatory behaviour is something else what we saw in which bismuth films and particles due to the quasi-2D sub-bands passing across the Fermi level. Also because of the small Fermi momentum, the chance of phonon scattering is very low. Hence bismuth has an extremely long phonon mean free path at low temperatures (~mm at 4.2K).

We have actually tried to synthesis bismuth nano particles with dimensions comparable to a Fermi wavelength, which cause the energy band quantization because of quantum confinement. It is means that as the size of the bismuth structure decreases, the speed at which the conduction band shifts up will be faster than that of the valence band. At a certain point, a gap opens up, and the semimetal-semiconductor transition should happen.

On the other hand, existence of the surface states may smear out any sharp features of the transition and magnetotransport which causes some problems in the carrier concentration due to dependency on temperature treatment, and an imperfect compensation between the majority bands. The insulating-like behaviour of the bulk bismuth respect to metallic behaviour on bismuth surface is so challenging problem for researchers and still need to be studied so much.

However, in the nano scale limit, the problem may get simplified by the fact that all the carriers are in the lowest Landau level at sufficiently low temperatures which can be understood by examining the Landau band structure of bismuth in the ultra-quantum limit field (For more details see [1-3]).

The nano particles of bismuth which shows a dependency on quasi-2D sub-bands which can be due to quantum confinement or quantum size effect, so-called Semimetal-to- Semiconductor (SMSC) transition. It may cause the shifting of the energy in the lowest electron sub-band.

The crystal structure of the Bi nano particles has been characterized by XRD and AFM techniques. The main point is that the obtained results show that some small atoms due to p – type silicon substrate in sol – gel method rapidly diffuses into the bismuth, giving rise to a film with large-crystal grains oriented with trigonal axis perpendicular to the plane of the film and having magnetotransport properties comparable to those grown by electro-depositions [6-8] like boron atoms.

Experimental procedure and discussions

The sol-gel process is commonly applied to synthesis such Bi materials owing to its several advantages such as low temperature processing and the ability to prepare materials in various shapes, compared with the conventional preparation procedures of glass and ceramics [9,10]. In this work we prepare Bi by using hydrolysis procedure of $BiCl_3$ and $Fe(NO_3)_3$ - which is transformed to rhombohedral phase by heating it at 500 ^{0}C. It obviously depends on the preparation procedures and Bi content in combination. By adding more Bi to silicon oxide matrix, the obtained powder trend to crystalline structure.

For synthesising the nano scale materials of Bi gel, 0.02 mol $BiCl_3$. $5H_2O$ and 0.02 mol $Fe(NO_3)_3$. $9H_2O$ are made a solution and transferred into the 30% dilute nitric acid. This transparent solution is then evaporated in a bath at 500^{0}C and the Bi nano particles are finally formed. Furthermore, Tetraethyl-Orthosilicate (TEOS) (Merk, > 99) is hydrolyzed with di-ionized water in that ethanol. Ethanol acts as a mutual solvent. TEOS, in ethanol is hydrolyzed with water containing acetic acid at room temperature for 30 min. The solution is then mixed with bismuth nitrate ($Bi(NO_3)_3$.) and iron nitrate ($Fe(NO_3)_3$) at 0 ^{0}C in specific molar ratio to obtain various content of Bi. After 30 min stirring at room temperature, the sol is vibrated for 20 min in ultrasonic bath to deconglomerate particles and then relaxed at room temperature for 30 min. The sol is stirred at 60 ^{0}C until it becomes gel and removes ethanol (about 24 hours). After gelatin, samples are dried at 60^{0}C to remove water and acetic acid and leave a transparent lump depend on Bi content. After that the lump samples are milled with mortar and calcinated at 500^{o}C. The thermal gradient during experiments procedure is 5 deg/min and the samples are put

in oven during 2 hours at calcinations temperature stated above. The procedure is shown in figure1.

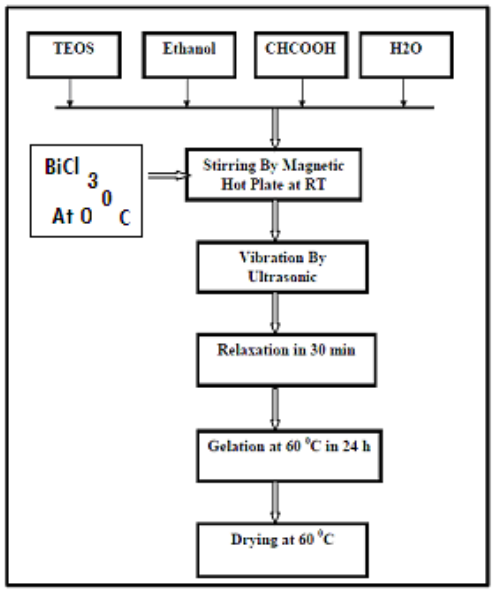

Figure 1: Flowchart of sol – gel process.

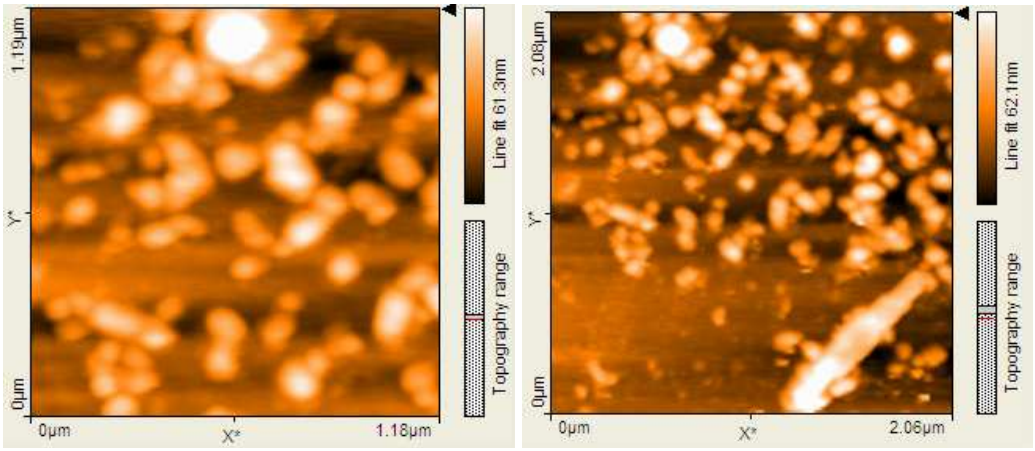

Figure 2: 2D - AFM microstructure of the Bi phase powder with different side views. The Bi nano particles look like dimer atoms on Si(100) 2 x 2 [11 -16].

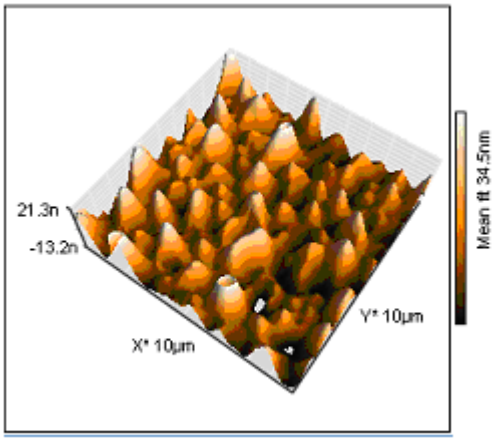

Figure 3: 3D - AFM microstructure of the Bi phase powder

Bi is synthesized at the calcinations temperature of 500^0C. The composition, structure and surface morphology of the Bi powder are investigated by AFM (The images are shown in figures 2 -5) and XRD (The patterns are shown in figures 6 – 7) techniques.

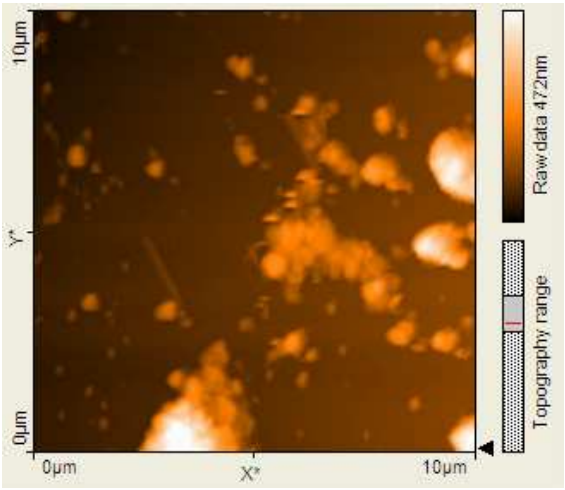

Figure 4: 2D (D: dimension) AFM microstructure of the Bi crystal phase after applying the magnetic field (1 Tesla).

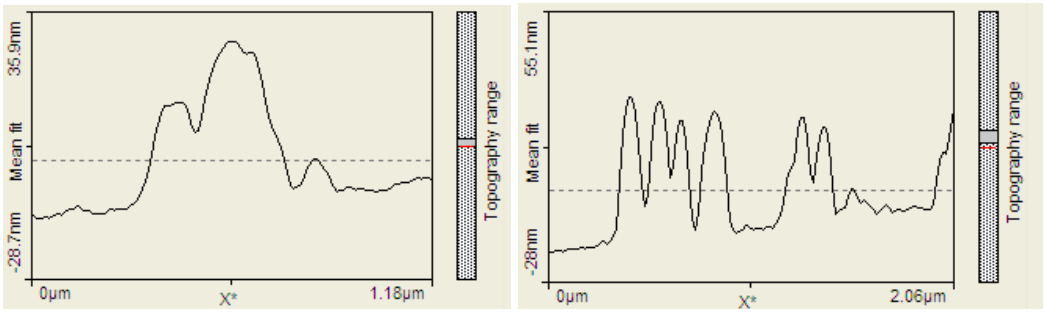

Figure 5: AFM microstructure topography shows different oscillating behaviour of surface states before (left) and after (right) applying magnetic field.

The sharp lines indicate that the film is well c-axis oriented. In this work, AFM is used to map different topographic features as shown in figures (2-5). This allows insight in the nano scale structure and the corresponding properties changes which relates to crystallographic and compositional changes. The AFM images obviously show much more detailed grain and nano structure analysis than XRD allows. In the topographic image in figures 2 and 4 bright colours (more peaks in figure 5 (right)), are high structures while dark colours (less peaks in figure 5 (left))are low structures due to different orientations of Bi grains (and the effect of magnetic field on the crystal phase of Bi). These different colours indicate different magnetic polarization (figures 2, 4 and 5) as found in [1,2], in where weak contrasts at the back ground with many large pores mean a weak magnetic field. By measuring the nano particles size, different grain sizes areas are found in the outer layer (100-150). It means different magnetic response and different amounts of pores. This leads to the assumption that the pores can change the nano structural properties of Bi as a suitable magnetotransport element in nano electronic devices.

In parallel to AFM technique, the XRD patterns in figures 6 and 7 show the Bi powders with 0.005 M nitric which annealed at 500^0C. XRD patterns are measured on a (GBC-MMA 007 (2000)) X-ray diffractometer and recorded with (K_α (Cu), 1.54 Å), 0.020 step size in where the

speed is 10 deg/min) radiation over a 2θ range of 10^0 – 60^0. Figures show the XRD patterns of some bismuth orientations as labelled in the figures such as (00l) planes. The range of Bi – nano particle's size is between 14 and 108 nm as determined by using X- powder method (figures 8-14) and Nanosurf Easy Scan 2-2 method (figure 15). Keep in mind that the small value of average grain size has been usually deduced from Scherer equation:

$$D = \frac{K\lambda}{\beta c \cos\theta}$$

Where D is the crystallite size of nano particle, k_α is a constant (0.94), λ is the wavelength of X-ray ($Cu_{k\alpha}$ = 1.5406 A°), β is the true half- peak width, and θ is the half diffraction angle of the centered of the peak in degree, but there is no more than one monolayer to be enough Brag layers for using Scherer equation. That is the main problem which causes to find two other measurements methods as addressed above.

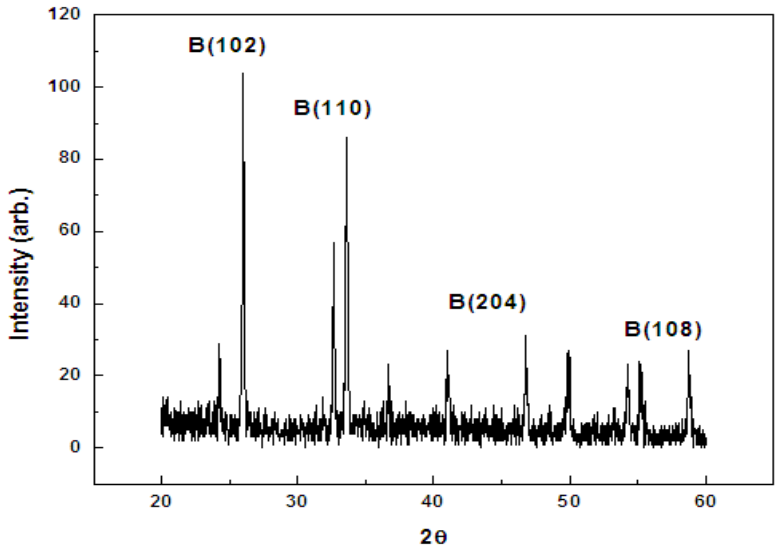

Figure 6: XRD patterns of the Bi powders before applying magnetic field at 500 °C.

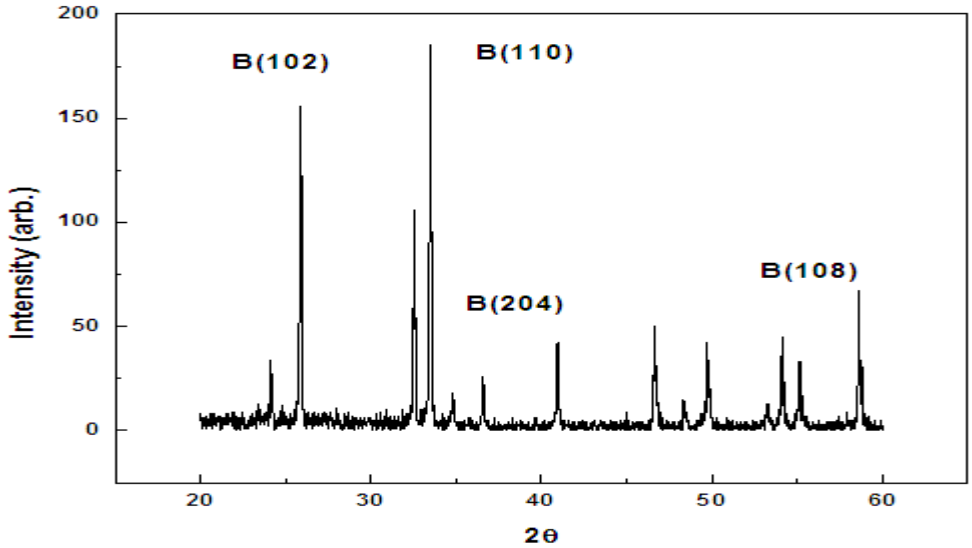

Figure 7- XRD patterns of the Bi powders with applying 1 T magnetic field at 500°C.

Strongest peaks at 17^0, 30^0 , 46^0 and 59^0 indicate B(102), B(110), B(204) and B(108), respectively. There are some broad and shadow peaks which show an amorphous structure of sample. Indeed, few broad peaks are also revealed in the background of XRD spectra, which are due to small size of Bi nano particles. Some lower intensity peaks around the main and huge peaks are completely removed after applying 1 T magnetic field. It could be attributed to weak bonds in this orientation and changeable crystalline state.

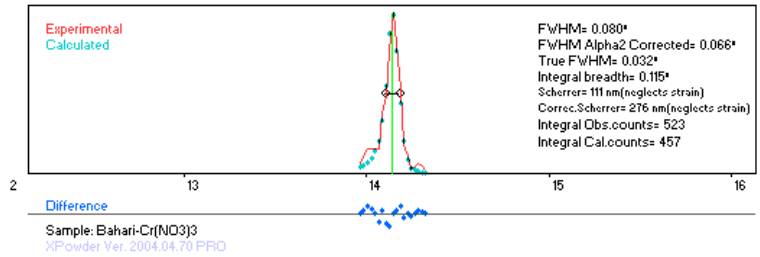

Figure 8: The size of nano particle is 27.6 nm as determined with using X- Powder method.

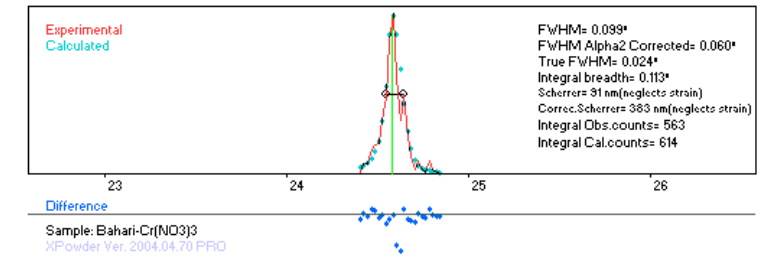

Figure 9: The size of nano particle is 31 nm as determined with using X- Powder method.

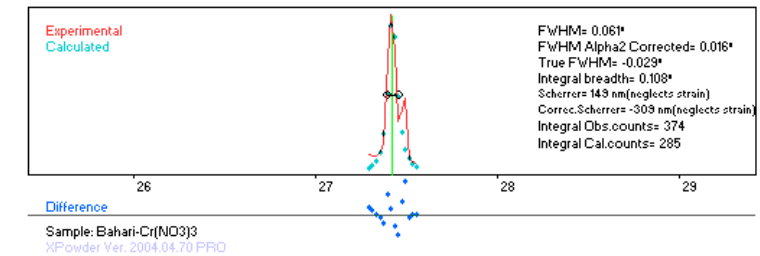

Figure 10: The size of nano particle is 14.3 nm as determined with using X- Powder method.

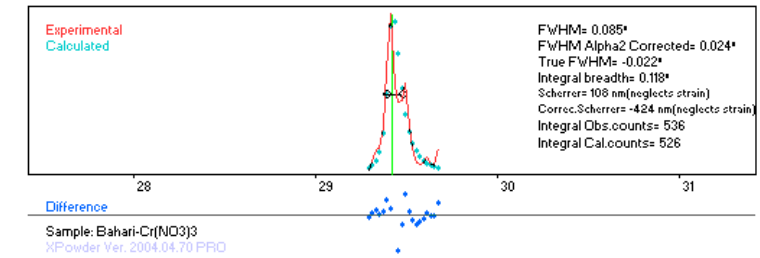

Figure 11: The size of nano particle is 108 nm as determined with using X- Powder method.

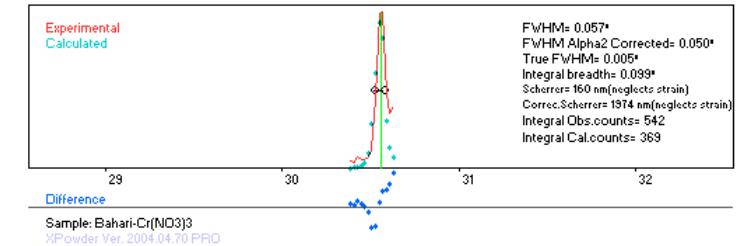

Figure 12: The size of nano particle is 16 nm as determined with using X- Powder method.

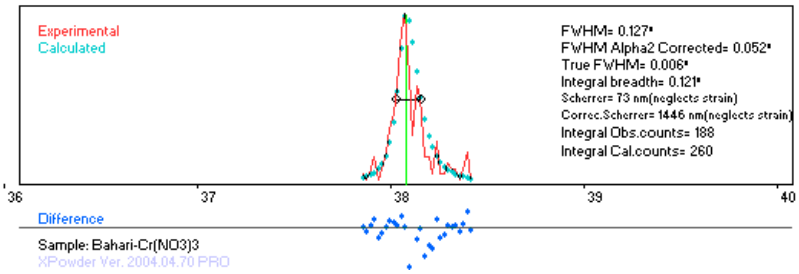

Figure 13: The size of nano particle is 73 nm as determined with using X- Powder method.

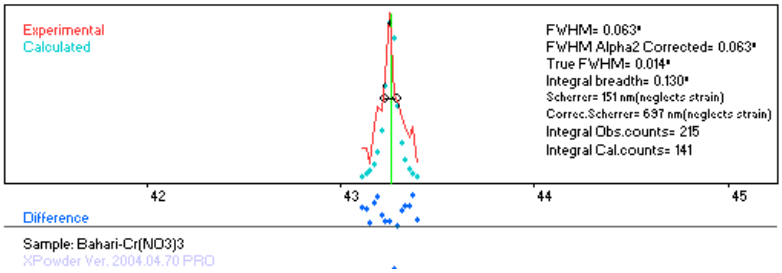

Figure 14: The size of nano particle is 151 nm as determined with using X- Powder method.

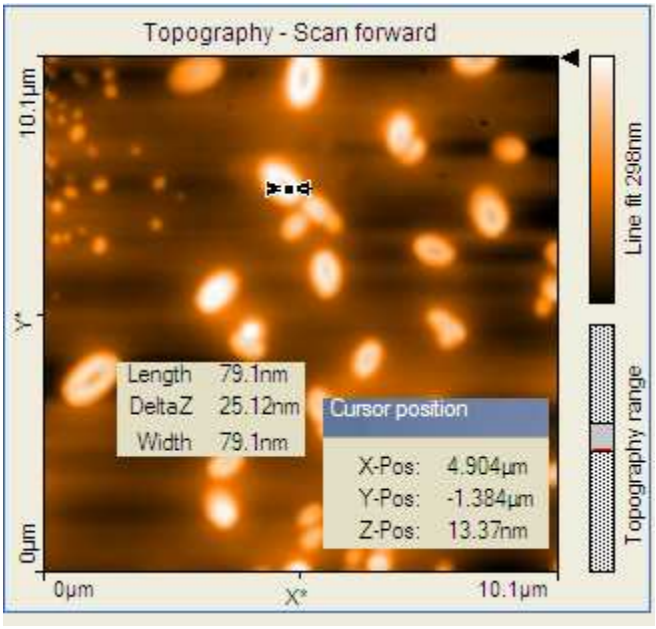

Figure 15: AFM image of the Bi powders with 0.005 M nitric acid at 500 °C. The size of nano particles is 79.1 nm as found by using Nanosurf Easy Scan 2-2 method.

CONCLUSION

We have studied the possible directions: the low dimensional bismuth nano-structures, and the physics and applications of the strong spinorbit coupling in bismuth. The Bi nano structural morphology and phases are studied by using XRD and AFM techniques and the obtained results indicate that further decreasing the dimensionality, it is found it has very long phonon mean free path, which makes it a good system for studying ballistic transport in one and zero dimensional systems.

Bismuth is thus a promising candidate for studying such structures mainly because bismuth has a very long Fermi wavelength. This makes it relatively easy to get reduced dimensionality without pushing the limit of the lithography technique too much.

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