Studies of preparing method of nano grain metal-insulator film Cu:CaF_2^*

Zhao Zi-Qiang (赵子强), Wei Lun-Cun (韦伦存), Wang Hao (王 浩), Zhong Yun-Cheng (钟运成) and Lu Xi-Ting (卢希庭)

(Institute of Heavy Ion Physics, Peking University, Beijing 100871)

Abstract A machine to prepare nano grain metal-insulator films, for example Cu:CaF_2 film, by means of magnetron sputtering generating clusters and at the same time evaporating insulator medium, is introduced. This machine is suitable for almost all solid metal and semiconductor clusters. And with it, many kinds of function film series can be prepared. The size of cluster embedded in insulator is from 10 to 70 nm. The Cu cluster and medium CaF_2 are both polycrystalline structure.

Keywords Embedded cluster, Crystalline structure, Nano grains, Film, Megnetron sputtering, Evaporating

1 Introduction

Cluster study is one of the hotest topics in recent years. The size of cluster is controlled to vary from several to several hundred angstroms. Cluster, as an intermediate between single atom and bulk material, has been studied.[1] Now, because of cluster embedded in medium possessing peculiar optical and electronic properties, it causes more interest.[2] In recent years, metal or semiconductor clusters prepared by using modern crystalline growth and ion implantation technologies have shown quantum effect, so they possess lots of novel physical properties, such as strong nonlinear response,[3,4] which can not be found in nature. Those composite materials can be used as nonlinear wave guide, fast light-electric responding materials, wide-band filter and so on. In general, the metal-insulator film is prepared by sputtering or coevaporating two kinds of materials on the substrate, then by fast heat treatment. This machine was based on the principle of magnetron sputtering generating clusters proposed by H. Haberland *et al.*[5] But, one evaporating source has been added in our machine. We first realize to prepare directly embedded clusters by magnetron sputtering generating metal cluster, and evaporating insulator medium simultaneously without heat treatment. The size of cluster can be controlled by discharge pressure. In principle, one can get many composite films by choosing different metals and insulator media.

2 Experiment and results

Fig.1 shows the sketch map of experimental setup, consisting of three parts: (I) magnetic controlling sputter region, (II) balance pressure region, and (III) evaporated and deposited region. The distance between two sputter targets with 100 mm in diameter, 5~10 mm in thickness, is controlled to vary from 30 to 50 mm. The sputter voltage is about 400 V with electric current of 1~2A. The pressure of discharge gas Ar is 25~50 Pa. The sputtered atoms or clusters form bigger clusters by colliding each other. Along with work gas, they pass the first diaphragm and enter the balance pressure region, where the pressure is kept at 5 Pa by oil enhanced pressure pump and a large part of work gas is pumped out. The cluster beam continues going forward through the third diaphragm, then enter the evaporated and deposited region, where the pressure is kept at 0.1 Pa by molecule pump. The clusters, embedded by evaporated medium material CaF_2, deposit onto silica substrate and form embedded cluster film.

With different material targets, variable composite nano-grain films have been successfully prepared, such as Cu:CaF_2 Ti:CaF_2 and

*The Project Supported by National Natural Science Foundation of China
Manuscript received date: 1996–04–16

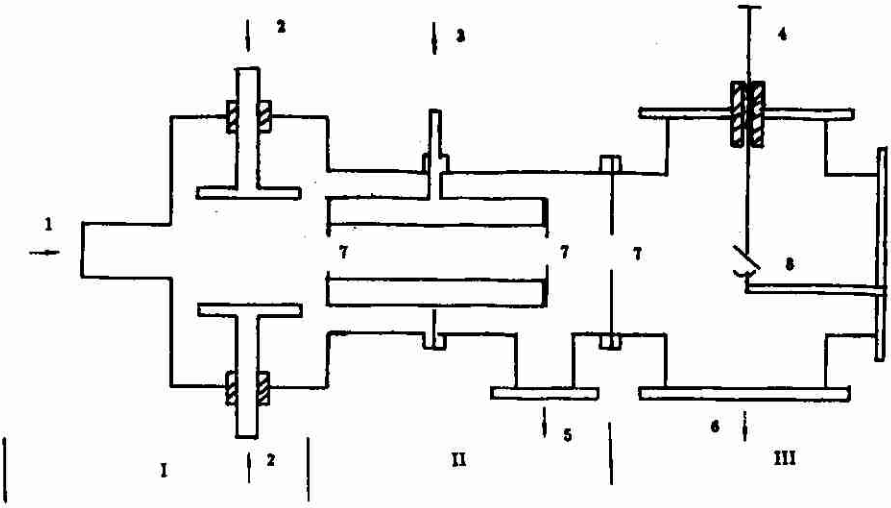

Fig.1 The sketch map of our machine to prepare nano grain metal-insulator films
1 Gas inlet, 2 Water cooling, 3 Liquid nitrogen inlet, 4 Specimen stand, 5 Oil enhancing pressure pump, 6 Molecule pump, 7 Diaphragm, 8 Evaporation source

Al:CaF_2 films. The films were deposited on Formvar foil for SEM. The samples were examined using an 160 keV scanning transmission electron microscope. Fig.2 shows a pair of bright-field/dark-field(BF/DF) image and selected area electron-diffraction(SAD) pattern for Cu:CaF_2 on Formvar foil. The dark points in BF image, corresponding the bright points in DF, represent copper clusters embedded in CaF_2 medium. The SAD pattern exhibits polycrystalline rings from fcc metallic Cu and fcc crystalline CaF_2. The 1 st, 2 nd, 4 th and 5 th rings correspond to {111}, {200}, {220} and {311} crystalline planes of CaF_2. The 3 rd and 6 th rings correspond to {111} and {200} crystalline planes of Cu. The rings from CaF_2 are brighter than those from Cu. It indicates that CaF_2 embeds Cu clusters and so prevents Cu accumulating effectively. The volume fraction of Cu is about 1/2.

Fig.3 shows the TEMs of Cu:CaF_2 with different cluster sizes. The cluster size is controlled by altering discharge pressure and varys from 8 to 70 nm. With condensation of liquid nitrogen, larger clusters can be prepared. The relationship between cluster size and discharge pressure is shown in Fig.4.

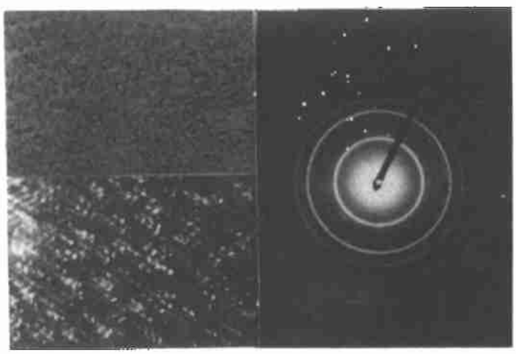

Fig.2 Bright- and dark-field TEM images and a selected-area electron-diffraction pattern for Cu:CaF_2 on Formvar foil

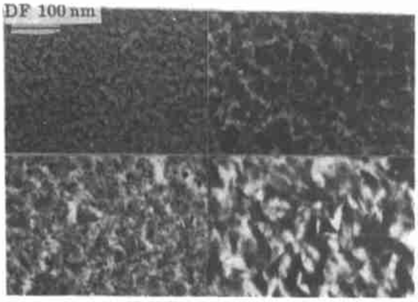

Fig.3 The bright-field TEMs of Cu:CaF_2 with different cluster sizes

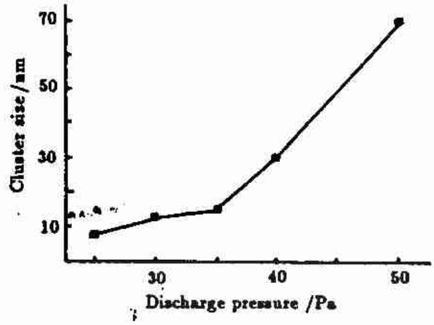

Fig.4 The relationship between cluster size and discharge pressure

3 Conclusions

With this machine, metal clusters embedded in insulator medium have been prepared. The TEMs of Cu:CaF_2 indicate: Cu clusters as well as CaF_2 are polycrystalline fcc structure. The size of Cu cluster can be controlled by changing discharge pressure. In addition, the electron-diffraction pattern of CuO was not found in SAD image. It indicates that the Cu clusters were well embedded in CaF_2 medium, which prevented Cu from oxidizing. It is very useful for not only studying cluster structure but also studying the physical properties of cluster. This machine is adaptable to prepare many kinds of cluster films. In principle, almost all solid metal or semiconductor cluster composite films can be prepared by changing sputter targets and evaporative materials. Those kinds of films possess lots of novel optical properties.

References

1 Wang Y, Suna A, Mahler W *et al.* J Chem Phys, 1987; 87:7315
2 Rubia A, Serra L. Phys Rev, 1993; B48:222
3 Chemla D S, Miller D A B. J Opt Soc Am, 1985; B2:1155
4 Rnox W H, Hirlimann C, Miller D A B *et al.* Phys Rev Lett, 1985; 54:1306
5 Habberland M, Karrais M. Clusters and cluster-assembled materials. In: Averback Robert S, ed. MRS symposium proceedings, Vol.206. 1991; 291