

Novel Preparation of Thin Films and Powders by Pulsed Ion Beam Ablation Plasma

Kiyoshi Yatsui, Weihua Jiang, Hisayuki Suematsu, Tsunetoshi Arikado, Tsuneo Suzuki
and Makoto Hirai

Extreme Energy-Density Research Institute, Nagaoka University of Technology, Nagaoka, Niigata 940-2188

Fax: 81-258-47-9890, e-mail: yatsui@nagaokaut.ac.jp

If an intense pulsed ion beam is irradiated on solid target, high-density ablation plasma is produced because the energy density will be high due to short range in the target. In 1988, the author proposed and demonstrated quick preparation of ZnS thin films by the ablation plasma, named intense pulsed ion beam evaporation (IBE). The preparation has been carried out without substrate heating and post-annealing, in a vacuum, with the instantaneous deposition rate of 1 cm/s. Good stoichiometry has been kept between the target and the thin films. The preparation of many kinds of thin films will be presented on, e.g., (Ba, Sr)TiO₃, B₄C, YBa₂Cu₃O_{7-δ}, In-Sn-O, SrAl₂O₄: Eu, Dy and Si_{1-x}Ge_x. Moreover, such high-density plasma provides to synthesize nanosized powders, by rapid cooling with the ambient gas. By various combinations of the target and the gas, we have succeeded in the synthesis of powders of Al₂O₃, AlN, TiO₂, TiN and Si. In the Si powders, the light emission of various color was observed by photo luminescence measurements. From above results, fruitful application seems to be available by the high-density ablation plasma produced by pulsed ion beam.

Key words: ion-beam evaporation, thin films, nanosized powders, ablation plasma

1. INTRODUCTION

Various thin films and powders with their size of several tens of nanometers have been prepared by many methods and used in electronic devices. Except solution-precipitation methods including spin/dip coating, most of the thin films and powders were prepared in a chamber by supplying raw materials of gaseous phases. Not only reactive chemical agents but also plasma are widely used as the gaseous phase to form thin films or powders. Sputtering is one of the most well known methods to prepare thin films. The apparatus of sputtering generates low-density and thermally non-equilibrium plasma. In the plasma, since electron temperature is higher than those of ions, high energy electrons may trigger damaging of the thin films. Comparing to the non-equilibrium plasma,

equilibrium plasma involves electrons and ions with comparable temperatures. Thus, it is not likely that the damage of thin films by high-energy electrons must be neglected.

Among thin films preparation methods utilizing equilibrium plasma, arc discharge is known. Since dc current is used for the discharge, most of the input energy is dissipated in electrodes and not used for the evaporation and ionization of the target materials. Thus, other highly-energy efficient plasma generation methods must be developed utilizing pulse current.

One of the present authors proposed a new method to prepare thin films at low temperature in 1988 by using high density ablation plasma produced by the pulsed ion beam interaction with solid targets, called pulsed ion-beam evaporation (IBE)[1,2]. Quick preparation has been available with good stoichiometry.

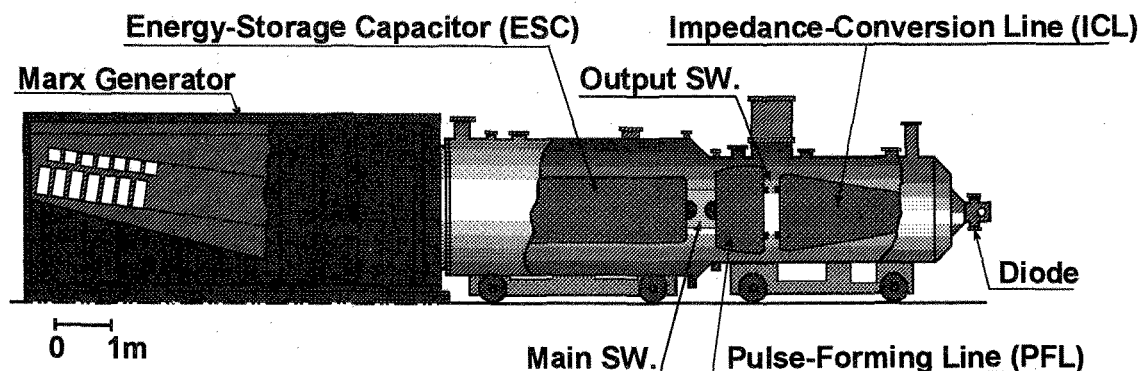


Fig.1 Schematic diagram of pulsed ion beam generator 'ETIGO-II'.

Furthermore, no external substrate heating nor sample annealing are not required to prepare crystallized thin films.

Using IBE, we have succeeded to prepare various thin films and nanosized powders[3]. Among them, TiFe hydrogen storage alloy thin films, which have never been obtained by other methods[4]. Furthermore, $B_{12+x}C_{3-x}$ thin films[5,6] and Si nanosized powder[7] prepared by IBE exhibiting unique characteristics, which have not been yielded by other samples. In this paper, preparation and characterization of $B_{12+x}C_{3-x}$ thin films and Si nanosized powder are reviewed.

2. ION-BEAM EVAPORATION METHOD

For preparation of thin films and nanosized powders, solid targets are irradiated by a pulsed ion beam. Schematic diagram of the pulsed ion beam generator is shown in Fig. 1. A Marx generator, which consists of 80 capacitors, is charged by an external power supply and connected to a energy-storage capacitor, a pulse-forming line and a impedance-conversion line to form pulsed current with pulse width of 50 ns. Typical operating condition for the ion-beam evaporation is accelerating voltage of 1 MV(peak), current of 60 kA.

The end of the impedance-conversion line is connected to a cathode and an anode of an ion-beam diode. Schematic diagram of ion-beam diode and thin film/nanosized powder preparation chambers are shown in Fig. 2. The ion diode used was a magnetically insulated diode (MID), where the motion of electrons is magnetically insulated by the transverse magnetic field. Using a polyethylene sheet as a flashboard anode, the ion species are mostly protons more than 75 %, which was diagnosed by energy spectrometer. By irradiating the pulsed ion beam with energy density of 10 to 100 J/cm² onto solid targets, high density ablation plasma is formed. Substrates are kept at temperature of 25 °C for thin film preparation and at -10 °C for nanosized

powder preparation. Thin films or nanosized powders are deposited on the substrates. Typical deposition rate is 0.1 to 0.5 $\mu\text{m}/\text{shot}$.

3. PREPARATION OF THIN FILMS AND NANOSIZED POWDERS BY IBE AND THEIR PROPERTIES

3.1 $B_{12+x}C_{3-x}$ thin films and their thermoelectric properties[5,6,8]

Boron carbide ($B_{12+x}C_{3-x}$) is known as a hard material whose Vickers hardness exceeds 5000. Bulks of $B_{12+x}C_{3-x}$ have been used in not only for mortars for crushing apparatus but also control rods in nuclear fission reactors.

Electronic properties of $B_{12+x}C_{3-x}$ are also unique. Since $B_{12+x}C_{3-x}$ is a semiconductor, Seebeck coefficient of $B_{12+x}C_{3-x}$ is higher than those of metals. Furthermore, because of its high melting point, the height in Seebeck coefficient is kept up to high temperature. This is the reason why $B_{12+x}C_{3-x}$ is thought as a candidate material for thermoelectrics.

In order to use $B_{12+x}C_{3-x}$ in electronic materials, preparation of $B_{12+x}C_{3-x}$ thin films are required. Thin films of $B_{12+x}C_{3-x}$ were prepared by chemical vapor

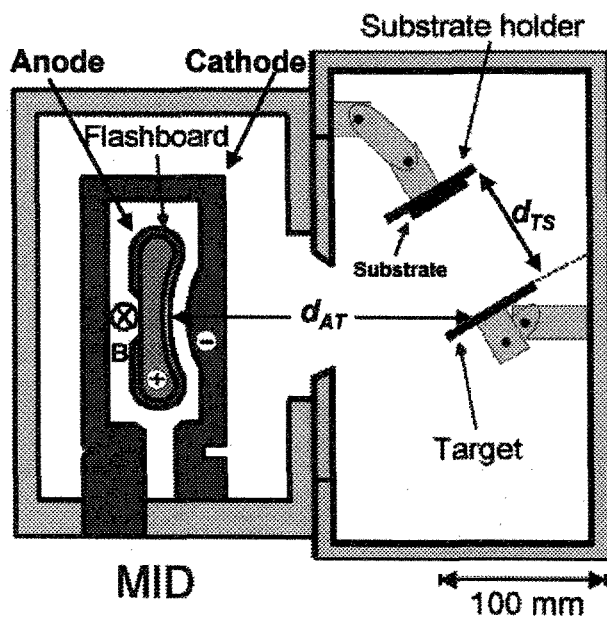


Fig. 2 Schematic diagram of ion-beam diode and thin film / nanosized powder preparation chambers.

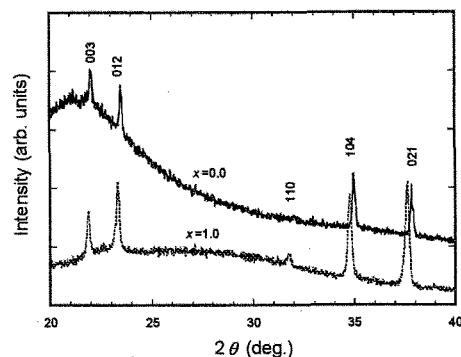


Fig. 3 XRD patterns for $B_{12+x}C_{3-x}$ thin films with nominal composition of $x=0.0$ and 1.0



Fig. 4 HRTEM image and diffraction pattern of a $B_{12.0}C_{3.0}$ thin film.

deposition (CVD) [9-12] and plasma spray [13]. During these processes, sample annealing or substrate heating were needed to crystallize $B_{12+x}C_{3-x}$ phase otherwise amorphous $B_{12+x}C_{3-x}$ thin films were prepared. For electronics applications, heat flux, to which the thin films are subjected, should be minimized. Thus, preparation of $B_{12+x}C_{3-x}$ thin films have been attempted by IBE.

Targets for the thin film preparation were sintered in a spark plasma sintering apparatus. Nominal composition of the targets were $x = 0.0$ and 1.0 . Using the targets, thin films were deposited by IBE on soda lime or quartz glass substrates. Phases in the thin films were identified by X-ray diffractometry (XRD) and high resolution transmission electron microscopy (HRTEM). Thermoelectric properties of the thin films were measured.

After 10 shots of ion beam bombardments on the targets, thin films were deposited on the substrates. The XRD patterns for the thin films were shown in Fig. 3. There are broad peaks at 21 and 25° for thin films prepared with $x = 0.0$ and 1.0 targets, respectively. They are peaks from the substrates. Except these peaks, all peaks corresponds to those for a $B_{12+x}C_{3-x}$ phase. Since no other peaks are seen in the XRD patterns, it is apparent that single phase $B_{12+x}C_{3-x}$ thin films were obtained by IBE at room temperature.

The peaks for $B_{13.0}C_{2.0}$ thin film are shifted to lower diffraction angles than those for the $B_{12.0}C_{3.0}$ thin film. In $B_{12+x}C_{3-x}$, as x increases, both a and c parameters increase [14]. The composition estimated from lattice parameters of the $B_{12+x}C_{3-x}$ thin films are comparable to the nominal composition of the targets. Furthermore, composition of a $B_{12+x}C_{3-x}$ thin film prepared by IBE with a $B_{12.0}C_{3.0}$ target had already been measured by electron energy loss spectroscopy (EELS) to be $B_{12.3}C_{2.7}$, which is comparable to that of the target [5]. Thus, $B_{12+x}C_{3-x}$ thin films with different composition, which should be close to that of the targets, were prepared.

A HRTEM image for the thin film prepared with the $x = 0.0$ target is shown in Fig. 4. All lattice spacings corresponds to that of $B_{12.0}C_{3.0}$, this grain was crystallized $B_{12.0}C_{3.0}$. Volume fraction of an amorphous $B_{12+x}C_{3-x}$ phase, which has been observed in B-C thin films prepared by CVD but is difficult to detect by XRD, must be small.

Electric conductivity (σ) and Seebeck coefficient (α) for these thin films were measured. Power factor, defined by $\alpha^2\sigma$, was calculated and plotted on Fig. 5. The highest value was obtained for the $B_{13.0}C_{2.0}$ thin film to be $8 \times 10^{-5} \text{ Wm}^{-1}\text{K}^{-2}$. Power factor for other $B_{12+x}C_{3-x}$ samples are also plotted on Fig. 5 for comparison. One of the present thin films exhibited more than twice as that of the highest power factor of $B_{12+x}C_{3-x}$ samples ($3 \times 10^{-5} \text{ Wm}^{-1}\text{K}^{-2}$) [15].

3.2 Si nanosized powders and their photoluminescence properties [7]

Although silicon does not emit light because of its indirect transition, it is known that light emission might be available from nanosized powders of silicon possibly due to quantumized confinement. In fact, several authors have reported light emission. From such a

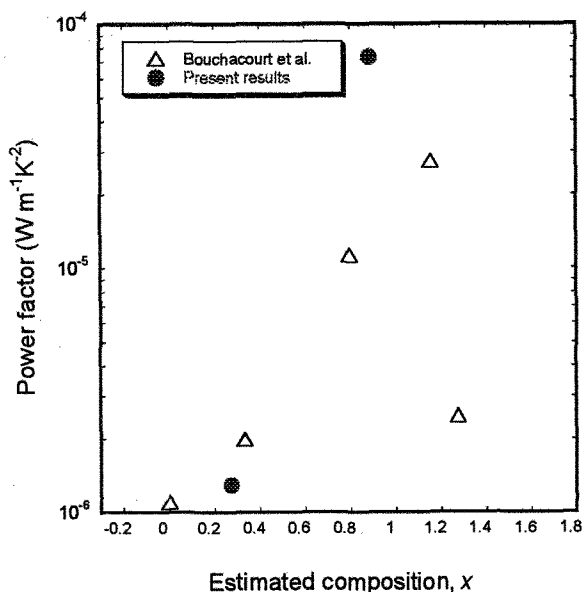


Fig. 5 Power factor of $B_{12+x}C_{3-x}$ thin films.

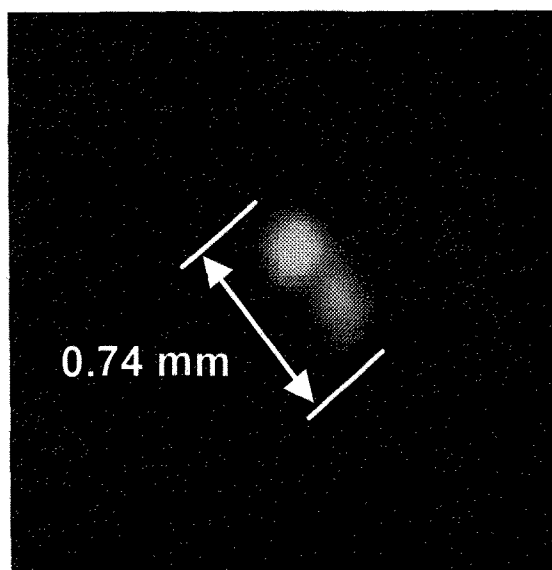


Fig. 6 Photoluminescence from Si nanosized powder prepared by IBE.

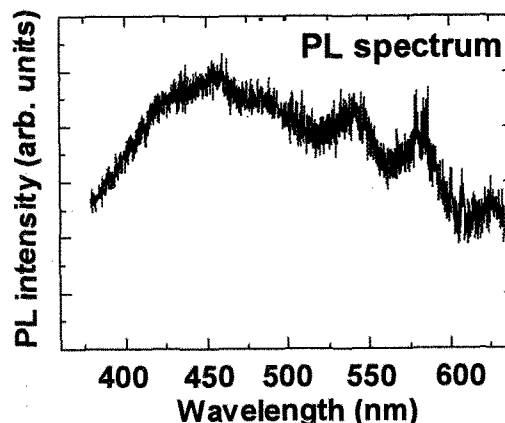


Fig. 7 Photoluminescence spectrum for Si nanosized powder prepared by IBE.

viewpoint, we have attempted to obtain light emission from nanosized powders of poly silicon. Here, nanosized powders was produced by the rapid cooling of the ablation plasma obtained by IBE on quartz glass substrates at -10°C in He gas at 1 Torr. Photoluminescence was measured by illuminating the nanosized powders by a He-Cd laser with wavelength of 325 nm. Finally, the nanosized powders were observed by HRTEM.

Photoluminescence from the Si nanosized powders is shown in Fig. 6. Bluish light emission is clearly seen. Photoluminescence spectrum of the emission is shown in Fig. 7. Light emission near the wavelength of 440 nm can be observed. In most of Si nanosized powders, the emitting light ranging from red to yellow. It was also reported that visible light emission was observed in Si nanosized powder with grain size less than 6 nm. Furthermore, wavelength of the photoluminescence decreased with decreasing particle size of Si nanosized

particles. Thus, grains of the Si nanosized powders prepared by IBE was observed by HRTEM. An HRTEM image of Si nanosized powder in Fig. 6 is shown in Fig. 8. Although a large grain with size of 10 nm exists, most of the grains are less than 5 nm. This result was almost in accordance with the former results. Furthermore, the blue photoluminescence was also observed after keeping the sample for 4 month in air. It is reported that samples emitting blue photoluminescence light were easily degraded and the blue photoluminescence did not emit for a long period. By using IBE, we have succeeded to develop highly stable Si nanosized powders which could emit blue photoluminescence.

ACKNOWLEDGEMENTS

The authors acknowledge Y. Bando and K. Kurashima in National Institute for Materials Science

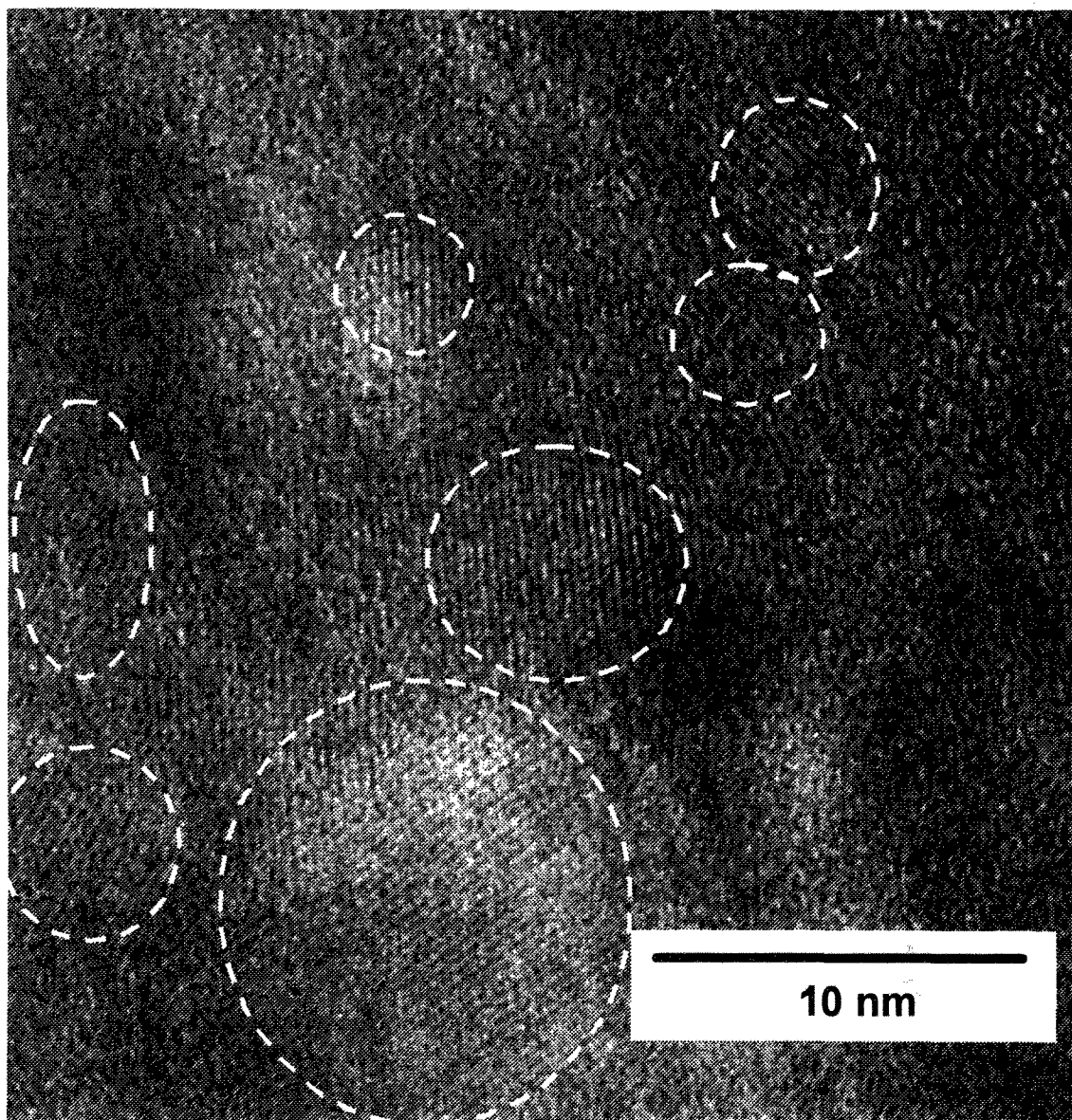


Fig. 8 HRTEM image of Si nanosized powder. White dotted lines indicate grain boundary of

and T. Yatsui and M. Ohtsu in Tokyo Institute of Technology for helping EELS and photoluminescence measurements. This work was partly supported by New Energy Development Organization, Grant-in-Aide for Scientific Research and the 21st Century COE Program of Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES

- [1]. Y. Shimotori, M. Yokoyama, H. Isobe, S. Harada, K. Masugata and K. Yatsui, *J. Appl. Phys.* **63**, 968-970 (1988).
- [2]. K. Yatsui, T. Sonegawa, K. Ohtomo and W. Jiang, *Materials Chemistry and Physics* **54**, 219-223 (1998).
- [3]. D. J. Rej, H. A. Davis, J. C. Olson, G. E. Remnev, A. N. Zakoutaev, V. A. Ryzhkov, V. K. Struts, I. F. Isakov, V. A. Shulov, N. A. Nochevnaya, R. Stinnett, E. L. Neau, K. Yatsui and W. Jiang, *J. Vac. Sci. Technol., A* **15**, 2214 (1997).
- [4]. T. Suzuki, T. Saikusa, H. Suematsu, W. Jiang and K. Yatsui, *Surf. Coat. Technol.* in press (2002).
- [5]. H. Suematsu, K. Kitajima, T. Suzuki, W. Jiang, K. Kurashima, Y. Bando and K. Yatsui, *Applied Physics Letters* **80**, 1153-1155 (2002).
- [6]. H. Suematsu, K. Kitajima, I. Ruiz, M. Takeda, T. Suzuki, W. Jiang and K. Yatsui, *Thin Solid Films* **407**, 132-135 (2002).
- [7]. K. Yatsui, W. Jiang, H. Suematsu, F. Endo and S. C. Yang, *Proc. 14th Int. Conf. High-Power Particle Beams*, in press (2002).
- [8]. K. Kitajima, T. Suzuki, W. Jiang and K. Yatsui, *Jpn. J. Appl. Phys.* **40**, 1030-1034 (2001).
- [9]. K. Ploog, *J. Crystal Growth* **24/25**, 197-204 (1974).
- [10]. C. Wood, *Boron-Rich Solids*, Vol. 140 (American Institute of Physics, New York, 1986)pp.362-372.
- [11]. S. Lee, J. Maqurowski, G. Ramseyer and P. A. Dowben, *J. Appl. Phys.* **72**, 4925-4933 (1992).
- [12]. K. Koumoto, *Am. Ceram. Soc. Bull.* **73**, 84-87 (1994).
- [13]. Y. Zeng, J. Feng and C. Ding, *J. Mater. Sci. Technol.* **16**, 63-66 (2000).
- [14]. T. L. Aselage and R. G. Tissot, *J. Am. Ceram. Soc.* **75**, 2207-2212 (1992).
- [15]. M. Bouchacourt and F. Thevenot, *J. Mater. Sci.* **20**, 1237-1247 (1985).

(Received December 21, 2002; Accepted March 26, 2003)