ELSEVIER

Journal of Power Sources 60 (1996) 151–155

JOURNAL OF POWER SOURCES

Organic solid capacitor with conducting thin films as electrolyte by ion-beam-assisted deposition

J. Kyokane [a], K. Yoshino [b]

[a] *Nara National College of Technology, Yamato-Koriyama, Nara 639-11, Japan*

[b] *Faculty of Engineering, Osaka University, Yamada-Oka, Suita, Osaka 565, Japan*

Received 15 November 1994

Abstract

Ion-beam-assisted deposition of organic materials has been proposed for obtaining high-quality thin films. As an application of these thin films, we have fabricated a solid electrolytic capacitor with organic conducting films prepared by means of evaporation of the 7,7,8,8-tetracyanoquinodimethane (TCNQ) complex on porous oxidized aluminium (Al) plates under ion-beam irradiation. The quality of TCNQ complex films prepared by this method has been confirmed to be greatly improved compared with that obtained using the conventional evaporation method, giving high conductivity (5 S/cm^2). The solid electrolytic capacitor also exhibits a large capacitance per unit area and a good frequency impedance response.

Keywords: Ion-beam-assisted method; Organic conducting materials; Evaporated thin films; TCNQ complex; Solid electrolyte; Electrolytic capacitors

1. Introduction

Among various methods for the preparation of inorganic and organic thin films, the evaporation technique under vacuum is one of the most simple and convenient methods. To obtain films of the desired quality, various modifications of this method have been proposed [1–3]. For example, a technique utilizing ion beam or cluster ion beam has been developed for the preparation of inorganic thin films such as metals and semiconductors. This technique showed to increase the packing density, promote crystalline growth, control morphology, minimize pin holes, modify thin film stress, etc. In most cases, however, when the surface of the substrate is irregular with steps or pores, the use of a simple evaporation technique does not result in a uniformly deposited surface. It is also difficult to evaporate the material deep into pores at the surface.

In this paper, we report a simple technique to improve the quality of an evaporated organic thin film by ion-beam-assisted deposition. As an application of the improved thin films, we have fabricated a solid electrolytic capacitor using 7,7,8,8-tetracyanoquinodimethane (TCNQ) complex films obtained by this method.

An aluminium electrolytic capacitor with liquid electrolyte has been widely used as the electrical and electronic elements because of its large capacitance and low price compared with other capacitors. This electrolytic capacitor, however, has a large impedance in the high frequency region due to a low conductivity of the liquid electrolyte in which ionic transport contributes to conduction. Recently, therefore, an electrolytic capacitor, using conducting charge-transfer complex or conducting polymers as the solid electrolyte in which electronic carriers play role, has attracted much attention [4–9]. To establish high quality capacitors with large capacitance per unit area and wide frequency response of impedance, it is very important to put an organic conductor into small pores with a diameter less than several μm formed on oxidized metal plates. It is not easy to obtain such capacitors by simple evaporation techniques.

In this study, we proposed a new technique utilizing ion-beam irradiation during the preparation of solid electrolyte by evaporation.

2. Experimental

The ion-beam-assisted deposition method has been utilized as follows. A Kaufman-type ion source of 5 cm in beam diameter [2] was prepared. The ion source was set in the vacuum chamber so that an ion beam can bombard the substrate at an arbitrary angle from the normal axis to the substrate, as schematically shown in Fig. 1. Al substrates with deep pores were set on the plate. The surface of an Al substrate was oxidized to Al_2O_3 of 700 Å in thickness. Oxidized Al

SSDI 0378-7753(95)02276-4

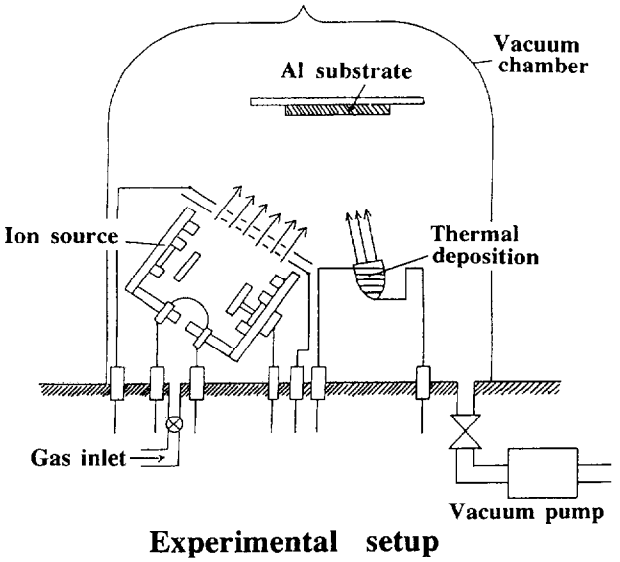

Fig. 1. Schematic setup of the ion-beam-assisted deposition method.

substrates with pores radii of 1.4 μm were used. The depth of the pores was about 100 μm. After the pressure in the chamber was set at 8×10^{-6} Torr, argon or nitrogen gas was let into the ion source until 1×10^{-4} Torr. During the evaporation of the sample on the substrate, the ion source was driven. Ion-beam energy and ion-current density were varied between 50 and 500 eV and 20 nA/cm^2 and 1 mA/cm^2, respectively. TCNQ was used as an acceptor. A charge-transfer complex formed between the TCNQ acceptor and various donors is known to exhibit high electrical conductivity originating from electronic transport. Among various donors an *N*-iso-propyl-4,4′-bipyridinium was prepared. The *N*-iso-propyl-4,4′-bipyridinium $(TCNQ)_n$ complex, whose molecular structure is shown in Fig. 2, was evaporated under ion-beam irradiation by heating to 240 °C in vacuum on the porous Al substrate. The capacitance and the frequency of these capacitors were measured by LCR meter (Ando: AG-4311) and impedance analyzer (Hewlett Packard: 4194 A), respectively.

3. Results and discussion

Before we utilized the ion-beam-assisted method, three kinds of simple methods were tried such as thermal deposition, corona charging deposition and deposition under ultrasonic wave irradiation using the Al plate with pores of 1.4 μm [10]. The maximum capacitances per unit area which

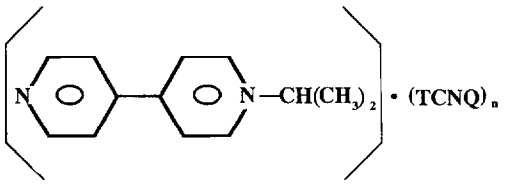

Fig. 2. Molecular structure of *N*-isopropyl-4,4′-bipyridinum $(TCNQ)_n$ complex.

Table 1
Maximum capacitance of the capacitors prepared by three simple deposition methods using the Al plate with 1.4 μm pore radii

	Thermal deposition	Deposition using corona discharge	Deposition under ultrasonic wave
Maximum capacitance (nF/cm^2)	100	380	560

were obtained with these methods are indicated in Table 1. With these methods, the maximum capacitance was as large as 560 nF/cm^2, which is about 30% of the capacitance obtained with liquid electrolyte. That is, a capacitance of 2 μF/cm^2 was realized by using the Al_2O_3 substrate with the same pores radius and liquid electrolyte. Therefore, in the next step, we studied the ion-beam-assisted deposition method to develop the improved solid electrolytic capacitor.

Fig. 3 indicates the capacitance of the capacitors, prepared with evaporated films on the Al plate with pores of 1.4 μm, versus ion-beam energy upon under constant-ion beam current using argon gas. From this figure it is evident that the capacitance depends on the ion-beam energy. The maximum capacitance was about 600 nF/cm^2 for the ion beams with energy of 100 eV and current of 0.07 μA/cm^2. Capacitance decreases at energies lower and higher than 100 eV. The radiation of ion-beam energy below 100 eV may be insufficient for driving TCNQ complex into the pores. The ion beam with energy much higher than 100 eV may sputter the deposited TCNQ complex again. However, the origin of this peculiar dependence of the capacitance on the ion-beam energy is not fully understood.

It should also be noted that the capacitance as high as 600 nF/cm^2 was obtained for an Al substrate with pore radius of 1.4 μm; this capacitance is much higher than the capacitance of the capacitor constructed utilizing films without ion-beam irradiation (100 nF/cm^2). These facts suggest that the TCNQ complex could be effectively deposited into the pores of the Al substrate by evaporation under ion-beam irradiation, resulting in a remarkable enhancement of the capacitance.

Capacitance versus ion-beam current under the constant ion-beam energy of 100 eV is shown in Fig. 4. The capaci-

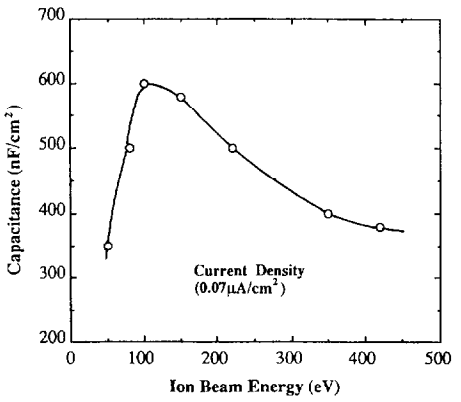

Fig. 3. Capacitance vs. ion-beam energy.

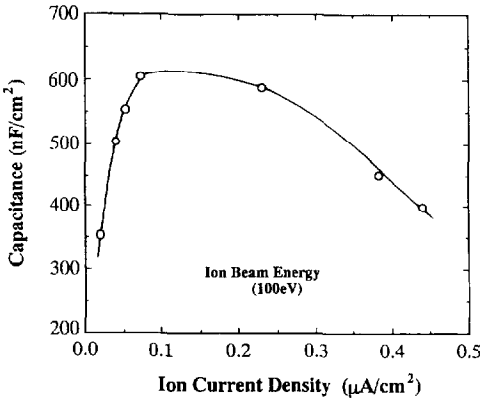

Fig. 4. Capacitance vs. ion-beam current.

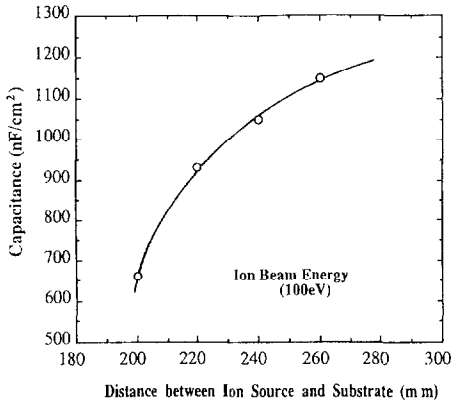

Fig. 6. Capacitance vs. distance between the ion source and the substrate.

tance is maximal in the range of ion-beam current between 0.07 and 0.3 $\mu A/cm^2$. In this region, crystallization was seen to progress. A similar effect was also reported in pyrene with the use of ion-beam irradiation [11].

It has been reported that in the case of growth of an inorganic film the ion–atom arrival ratio (n^+/n_0) plays an important role, where n^+ is the number of ions and n_0 is the number of evaporated atoms. Whether or not this relation is effective for organic materials has not yet been clarified. However, it is interesting to investigate whether this concept can be applied to organic materials, and especially to the enhancement of capacitance. We also put a shutter between the substrate and ion source in order to open the ion beam for the desired duration of time during evaporation. The maximum capacitance which has been obtained by changing both ion–molecule arrival ratios (n^+/m_0), where m_0 is the number of evaporated molecules, and the opening time of the shutter was 760 nF/cm^2.

Then, we modified the deposition apparatus as illustrated in Fig. 5. With this new method: (i) the central axis of both the melting pot and ion source coincide: (ii) the distance from the ion source to the Al substrate can be varied between 50 and 270 mm, and (iii) helium gas, as the ion beam, was let into the ion source .

Fig. 6 shows the dependence of the capacitance on distance from the ion source to the Al substrate under irradiation with the ion-beam energy of 100 eV and the ion-current density of 0.07 $\mu A/cm^2$. The capacitance increased rapidly by moving the substrate away from the ion source, and then saturated at a distance greater than 270 mm. An enhancement of capacitance is interpreted to be due to the fact that the direction of the motion of evaporated molecules is collinear with the ion beam and also the sputtering effect decreases with increasing the distance between ion source and substrate. Then, the evaporated molecules can penetrate with ion beam into the deep pores. In fact, such an enhancement effect was not observed when a non-collinear apparatus was used, see Fig. 1.

Fig. 7 shows the dependence of capacitance on the rotation speed of substrate for the ion-source substrate distance of 270 mm under ion-current density of 0.07 mA/cm^2 using helium gas. In this method we got a maximum capacitance of 1.38 $\mu F/cm^2$. This capacitance was the greatest among those

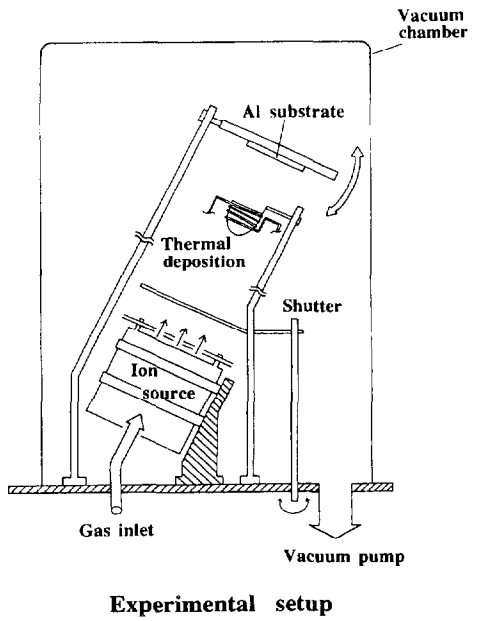

Fig. 5. Schematic setup using the improved ion-beam-assisted method.

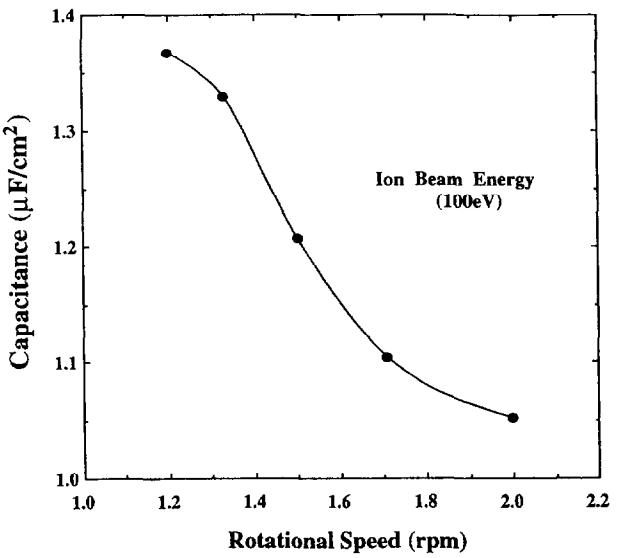

Fig. 7. Capacitance vs. rotation speed of the Al substrate.

obtained using the various deposition methods and was greater by more than one order of magnitude than the value of the capacitance obtained with a simple thermal deposition method. This capacitance obtained by optimized ion-beam-assisted deposition of TCNQ complex as solid electrolyte is comparable with that of a liquid electrolyte capacitor with the same Al substrate.

These capacitances depend strongly on the ion size. The maximum capacitances which were obtained with three kinds of ion beam (Ar^+, N_2^+, He^+) under the same conditions (ion energy of 100 eV, ion-current density of 0.07 $\mu A/cm^2$ and rotation speed of Al substrate at 1.2 rpm) are indicated in Table 2. To insert organic materials into tiny pores with a diameter of several μm, one might as well irradiate using helium ion beams with small size as use argon beams.

Fig. 8(a) shows the scanning electron microscope (SEM) figure of the evaporated TCNQ complex film which exhibited the maximum capacitance, and Fig. 8(b) gives the SEM picture of TCNQ complex film under non-irradiation conditions. From these figures, we see that the film prepared on the substrate with the helium ion-beam irradiation is very different from that without irradiation. The film obtained using the ion-beam-assisted deposition method seems to be much higher in density and uniformity. The film quality is remarkably improved by irradiation of the ion beam.

The frequency characteristics of the obtained capacitor by the present method and also of the commercially available electrolytic capacitor using a liquid electrolyte are shown in Fig. 9. This figure indicates that the frequency dependence of the capacitor prepared by ion-beam-assisted deposition is greatly improved and coincides well with that of an ideal capacitor, which should be originated from the increase of electrical conductivity in the electronic electrolyte. That is, the impedance of electrolytic capacitor is given by Eq. (1).

$$Z=\sqrt{(ESR)^2+(X_L-X_C)^2} \quad (1)$$

where ESR is the equivalent series resistance, X_L and X_C the inductive reactance and capacitive reactance, respectively. In the conventional capacitor, the frequency dependence of the impedance is controlled by a large equivalent series resistance in the frequency range between 10^4 and 10^6 Hz. Therefore, it is necessary to make the ESR as small as possible. In the present case, the high conductivity originating from the electronic conduction in the TCNQ complex plays an important role in contrast to the liquid electrolyte in which the ionic transport contributes mainly to conduction. The frequency characteristics of impedance are the same with those of the capacitors which are fabricated by using a fusible TCNQ complex and a conducting polymer as solid electrolyte

Table 2
Maximum capacitance with three kinds of ion beam

	Ar^+	N_2^+	He^+
Maximum capacitance (nF/cm^2)	850	1250	1380

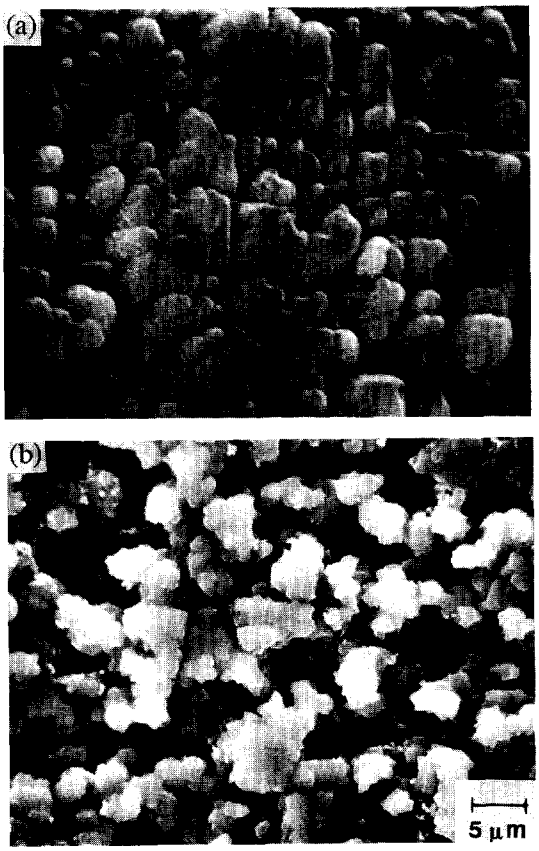

Fig. 8. SEM figures of TCNQ complex under (a) helium ion-beam irradiation, and (b) non-irradiation conditions.

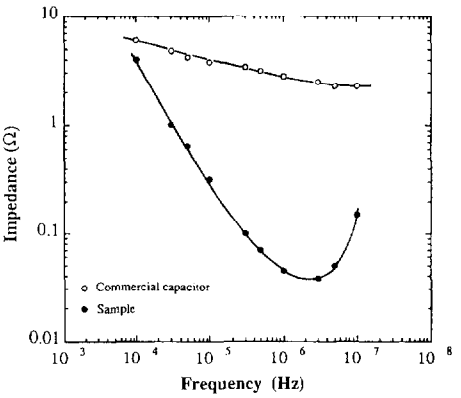

Fig. 9. Frequency characteristics of the obtained capacitor.

[4–6,8]. It should also be mentioned that the temperature dependence of the capacitance of the present capacitor utilizing the electronic solid electrolyte was much smaller and the dielectric loss was also small compared with those of a commercial capacitor with a liquid electrolyte.

4. Summary

The results of this study are summarized as follows:

1. A new method of the ion-beam-assisted deposition of organic materials utilizing the Kaufman-type ion source was proposed.

2. The quality of TCNQ complex films prepared by this method was confirmed to be greatly improved compared with that obtained with the conventional evaporation method.

3. The maximum capacitance was obtained in the range of the ion-beam current between 60 nA/cm^2 and 90 nA/cm^2 for the ion-beam energy of 100 eV under the ion source-substrate distance of 270 mm using helium ion beams.

4. Organic solid capacitors fabricated using the TCNQ complex by ion-beam-assisted method exhibited the ideal frequency dependence of impedance up to 10^6 Hz, contrary to the capacitor with the liquid electrolyte. Also, the evaporated TCNQ complex films confirmed to exhibit high electronic conduction.

5. The frequency characteristics are the same as those of the organic solid capacitors utilizing a fusible TCNQ complex and also conducting polymers.

Acknowledgements

The authors are very grateful to Dr Isao Isa and Mr Toshiro Maruyama for his supply of the TCNQ complex and the porous oxide Al plates.The present work is supported by a Grant-in-Aid of scientific research from the Ministry of Education, Science and Culture of Japan.

References

[1] T. Takagi: *Thin Solid Films, 92* (1982) 1.
[2] J.M.E. Harper, J.J. Cuomo, R.J. Gambino and H.R. Kaufman, in O. Aucell and R. Kelly (eds.), *Ion Bombardment Modification,* Elsevier, Amsterdam, 1984, Ch. 4.
[3] H. Usui, I. Yamada and T. Takagi, *J. Vac. Sci. Technol. A, 4* (1986) 52.
[4] S. Niwa, *Synth. Met., 18* (1987) 665.
[5] I. Isa, *Nikkei New Mater., 57* (1989) 48 (in Japanese).
[6] I. Isa, M. Fukuda, T. Hosaka, H. Yamamoto and K. Yoshino, *Trans. Inst. Electron. Inf. Commun. Eng. Jpn., J75-C-II, 10* (1992) 530 (in Japanese).
[7] H. Yamamoto, M. Fukuda, I. Isa and K. Yoshino, *Trans. Inst. Electron. Inf. Commun. Eng. Jpn., J75-C-II, 12* (1992) 745 (in Japanese).
[8] Y. Kudoh, S. Tsuchiya, M. Fukuyama, T. Kojima and S. Yoshimura, *Synth. Met., 20* (1991) 1133.
[9] J. Kyokane, I. Isa and K. Yoshino, *Jpn. J. Appl. Phys., 32* (1993) 1303.
[10] K. Yoshino and J. Kyokane, *Technol. Rep. Osaka University, 41* (1991) 10.
[11] M. Migita, H. Ishihara, T. Ishiba and A. Taniguchi, *Soc. Electron. Eng. Jpn, Insulator Res. Mater., EIM-84-50* (1984) 39 (in Japanese).