

Application of compact microwave ion source to low temperature growth of transition metal nitride thin films for vacuum microelectronics devices

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A compact microwave ion source was applied to the low temperature growth of transition metal nitride thin films for the cathode of vacuum microelectronics devices. An ion beam assisted deposition system consisted of a compact microwave ion source and an electron beam evaporator was developed. Depositions of zirconium nitride and niobium nitride thin films were performed and the film properties were investigated. As a result, it was found that polycrystalline films of zirconium nitride and niobium nitride were prepared at the substrate temperature as low as 500 °C, which was almost 200 °C lower than the results shown in the literature. The reason for this reduction of substrate temperature might be attributed to low gas pressure during deposition, due to the use of a single aperture ion source. The control of film composition by controlling the ion-atom arrival rate ratio achieved the control of work function. It was concluded that the ion beam assisted deposition with microwave ion source provides a possible process of cathode deposition. © 2000 American Institute of Physics. [S0034-6748(00)65202-4]

I. INTRODUCTION

It is well known that the use of ion beam provides thin films with superior property at a lower substrate temperature, especially for compound materials. So far, insulators such as silicon oxide and silicon nitride¹ and metallic compounds such as transition metal nitrides² have been prepared by ion beam assisted deposition (IBAD). Transition metal nitrides are generally expected as a hard coating material and also as a barrier metal in semiconductor devices, and the intrinsic natures of these materials such as chemical inertness, high melting point, large heat of formation, and high electric conductivity³ match the requirement of the cathode material of vacuum microelectronics (VME) devices. Here VME devices are micron-sized vacuum tubes with miniaturized field emission cathode fabricated by contemporary thin film and micromachining technologies.⁴ One of the serious problems of these devices is current fluctuation of emission currents. The emission stability of the bulk nitride cathode is known to be excellent,⁵ but little progress on deposited nitrides can be seen. This is entirely due to the difficulties in synthesis of the nitrides at the lower temperature. As described earlier, thin films of transition metal nitrides have been deposited by IBAD, but substrate temperature as high as 750 °C is still necessary to obtain the films with an adequately low electrical resistivity. In order to fabricate VME devices on glass substrate for application to flat panel displays, further reduction of the substrate temperature is necessary. We have applied the compact microwave ion source to the deposition of these films through IBAD.⁶ Since previous deposition² was performed under relatively high working pressure, we

thought that one of the possible factors to reduce substrate temperature is the lower working pressure. The ion source used in the present study has only one aperture, and the pressure difference could be easily achieved. As a result, we could deposit the polycrystalline zirconium nitride (ZrN_x) and niobium nitride (NbN_x) films at a lower substrate temperature. In this article, the film properties of these nitride films estimated from the viewpoint of cold cathode material, are given.

II. ION BEAM ASSISTED DEPOSITION OF TRANSITION METAL NITRIDES

A. Deposition system

Figure 1 shows the schematic diagram of the deposition system. The IBAD system consists of a compact microwave ion source⁷ and electron beam evaporator. To evaporate transition metal which has a relatively high melting point, an electron beam evaporator rather than a resistively heated evaporator is preferred. The ion source utilizes a permanent magnet for the axial magnetic field, and a closed magnetic circuit is formed with ferromagnetic materials. Owing to little leakage of magnetic field, little interference with the electron beam evaporator would be expected. The substrate holder is set above the electron beam evaporator and the ion source is settled at 45° off with respect to the vertical line. Adjusting the angle of the substrate holder, the ion incident angle was changed, but consequently the incident angle of the depositing metal atoms also changed. It is generally difficult to transport low energy ions effectively due to the space charge effect, thus we adopted an accel-decel type transporting system. The ion source has a single extraction aperture with a diameter of 2 mm. This single aperture enables us to deposit at a lower gas pressure, as described later.

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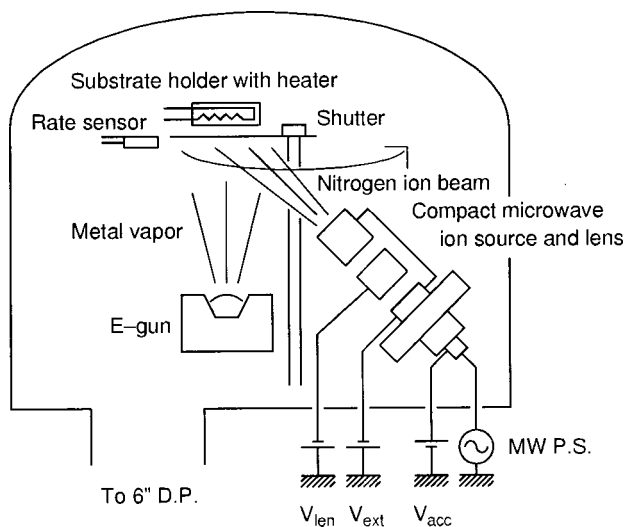


FIG. 1. Schematic diagram of the deposition system.

The ions are extracted once by a high negative potential of several kilovolts. The source possesses an einzel lens and the extracted ion beam can be converged. Deceleration was performed between the end electrode of the einzel lens and substrate holder. In such a system, neutralized ions with higher energy exist. Because these neutralized ions can significantly by damage the films, the substrate holder was located off axis of the ion source. The deposition rate could be monitored by a quartz oscillator. The entire system was pumped by a 6 in. oil diffusion pump and the residual gas pressure was about 2×10^{-4} Pa.

B. Deposition condition

The deposition conditions are summarized in Table I. We have deposited ZrN_x and NbN_x films on a p -Si(100) wafer with an ion-atom arrival rate ratio (ARR) and substrate temperature (T_s) as parameters. Here ARR was defined by the atomic flux of nitrogen to that of metal atom flux, assuming that the ion beam is composed of N_2^+ ions. This estimation is based on the experimental evidence that this ion source yields up to 25% atomic nitrogen ions and a negligible amount of doubly charged atomic ions.⁷ The presence of atomic ions causes an error of up to 20% in ARR, but the fraction varies with the operating condition; thus we did not take this effect into consideration. For the ZrN_x films, the ion energy and ion incident angle were varied. The nitrogen pressure during deposition was 2×10^{-3} Pa.

TABLE I. Deposition conditions for ZrN and NbN films.

| Terms | ZrN | NbN |
|-----------------------|------------------------------------|-------------------------------------|
| Evaporation rate | 0.05 nm s^{-1} | 0.03 nm s^{-1} |
| Ion energy | 200 eV, 500 eV, 1 keV | 600 eV |
| Ion current density | $6\text{--}18 \mu\text{A cm}^{-2}$ | $11\text{--}34 \mu\text{A cm}^{-2}$ |
| ARR | 0.3–0.9 | 0.2–2.0 |
| Substrate temperature | 120–650 °C | 200–600 °C |
| Ion incident angle | 45°, 22.5° | 22.5° |

III. FILM PROPERTY

A. Nitrogen composition

Nitrogen composition x of the deposited films was estimated by Rutherford backscattering spectrometry (RBS). As for the NbN_x films, x was controlled by controlling ARR. Although the absolute value of the nitrogen composition decreased slightly with an increase of T_s , x could be determined by ARR. The typical relation at T_s of 500 °C is: $\text{ARR}=0.3$, $x=0.3$, and $\text{ARR}=1.8$, $x=1.1$. For the ZrN_x films, zirconium silicide was formed occasionally, thus the relation between the ARR and x deviated. Nevertheless, x varied in accordance with ARR.

B. Crystallinity

Crystallinity was evaluated by x-ray diffraction. For both ZrN_x and NbN_x films exhibited amorphous structure when deposited at T_s lower than 400 °C. At T_s higher than 500 °C, the films tended to be crystallized. For NbN_x , the x-ray diffraction pattern showed formation of the different phases of Nb_2N , Nb_4N_3 , and NbN in accordance with x .⁶

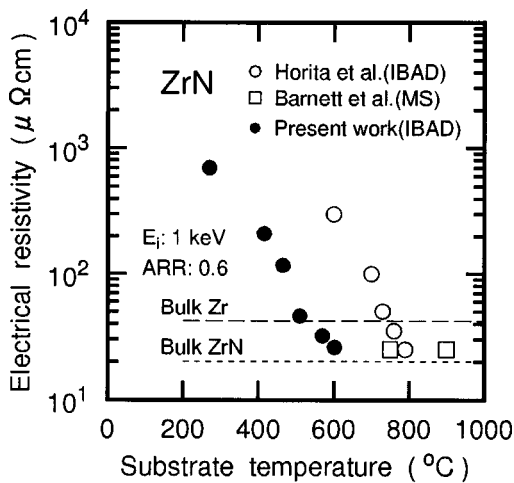
C. Electrical resistivity

Electrical resistivity was measured by a four point probe at room temperature. Figures 2(a) and 2(b) show the relation between T_s and the electrical resistivity for ZrN_x and NbN_x films, respectively. In Fig. 2(a), examples of the temperature dependence of the resistivity reported by Horita *et al.*² and also by Barnett *et al.*⁸ are also plotted. The former was performed by ion beam assisted deposition and the latter was performed by magnetron sputtering. As compared with these previous results, we could deposit film with similar resistivity at lower temperature by almost 200 °C. The lowest resistivity obtained in the present study was $25 \mu\Omega \text{ cm}$, and very close to bulk value.³ The nitrogen pressure during deposition was 10^{-2} and 10^{-1} Pa for the previous cases. The reason why our results showed lower temperature has not been clarified yet, but lower pressure in the deposition chamber may be related to this issue. In fact, deposition with nitrogen introduction around the substrate holder significantly affected the resulting film property, especially electrical resistivity.⁹ Oblique ion incidence of 45° showed better property. Low ion energy gave lower resistivity at lower T_s but the lowest electrical resistivity was obtained with the film deposited by a 1 keV nitrogen beam. For a detailed relation between the instrumental parameters and the film property, further investigation will be necessary.

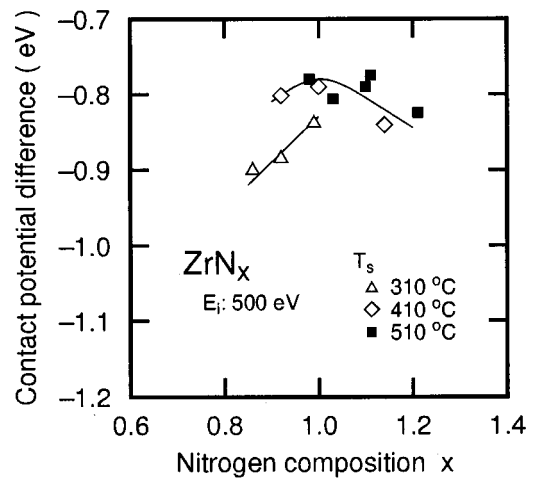
For NbN_x films, electrical resistivities were higher than the bulk values. At T_s of 500 °C, the electrical resistivity of NbN film was 400–600 $\mu\Omega \text{ cm}$, and that of Nb_2N was 200 $\mu\Omega \text{ cm}$.

D. Electron binding energy

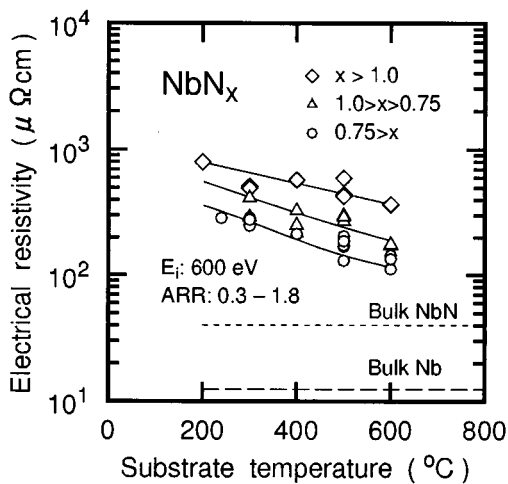
Atomic bonding was evaluated by x-ray photoelectron spectroscopy (XPS). Prior to measurement, the film surface was cleaned with 3 kV argon ion bombardment. Figure 3 shows a typical example of the Nb 3d electron binding energy of NbN_x film deposited with ARR of 1.0. The solid



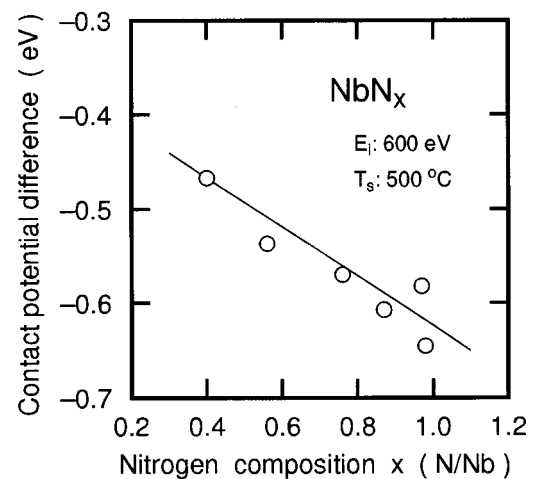
(a)



(a)



(b)



(b)

FIG. 2. Relation between substrate temperature and electrical resistivity: (a) ZrN films and (b) NbN films.

FIG. 4. Relation between nitrogen composition and work function: (a) ZrN films and (b) NbN films.

vertical line shows the peak position of metallic Nb $3d_{5/2}$. A chemical shift to 204.7 eV was seen both for the film deposited with T_s of 300 and 600 °C. This result shows nitriding was achieved even at the low T_s of 300 °C.

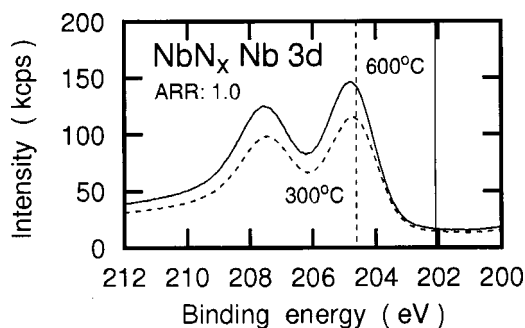


FIG. 3. X-ray photoelectron spectrum of Nb $3d$ electrons of NbN films.

E. Work function

Work function was evaluated by a Kelvin probe in air. The counter electrode was gold, thus the present result shows a contact potential difference between the sample and gold. The measurement in air does not give a physically meaningful value of work function, but actual VME devices are fabricated through multiple processes including exposure to air and even to acid. In operation, no flushing is generally performed unlike the field emission cathodes for the electron microscope, thus the contaminated surface may give us effective work function in practical operation. Figures 4(a) and 4(b) show the work functions as a function of nitrogen composition x , for ZrN_x and NbN_x , respectively. For ZrN_x , work function increased with an increase in x , below $x=1$ and tended to saturate at $x>1$, while for NbN_x , work function decreased with an increase in x . Bulk ZrN has higher work function than Zr and bulk NbN has slightly lower work

function than Nb,¹⁰ thus present results reflect the bulk property.

F. Endurance against low energy ion bombardment

We have checked the endurance of NbN_x films against 400 eV argon ion bombardment, because cathodes are generally subjected to bombardment of ions which are produced in a space by electron impact. As a result, total sputtering yield of the Nb film was about 0.4, and it slightly increased with an increase in the nitrogen composition. Total sputtering yield was about 0.46 for the NbN film. Taking the fact that sputtering yield of bulk Nb against 400 eV argon ion bombardment is 0.4,¹¹ the present values are considered to be low enough.

IV. SUMMARY

We have applied the compact microwave ion source to the low temperature growth of transition metal nitride thin films for vacuum microelectronics devices. As a result, it was found that polycrystalline films were obtained both for ZrN and NbN at a substrate temperature as low as 500 °C. Also the electric resistivity was sufficiently low at this temperature. We could control the work function of these materials, which has significant effect on the field electron emission.

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