ELSEVIER

Journal of Alloys and Compounds 330–332 (2002) 348–351

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Modification of electrical and optical properties of metal nitride thin films by hydrogen inclusion

Y. Hayashi*, T. Ishikawa, D. Shimokawa

Department of Materials Science and Engineering, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan

Abstract

Hydrogen atoms included in metals and compounds can modify the electrical and optical properties of the materials. Change of electronic properties of copper nitride and aluminum nitride by hydrogen ion implantation are studied as an example for the hydrogen induced modification of material properties. Electrical conductivity of copper nitrides increased more than two orders of magnitude by hydrogen implantation. Aluminum nitride remained insulating but the optical absorption coefficient increased. The modification may be considered due to the formation of impurity donor states in the band gap of the compounds. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen; Nitride; Copper nitride; Aluminum nitride; Electrical conductivity; Optical absorption

1. Introduction

Hydrogen can modify the physical properties of materials reversibly by charging and discharging. A dramatic example is a switchable mirror of yttrium hydrides [1–4], which depends on the metal–insulator transition of rear earth metal hydrides [5]. This effect is also known in rear earth metal–magnesium alloys [6,7]. Hydrogen in semiconductor materials mostly forms impurity donor states and acts to reduce the activity of both acceptor and donor dopants by making complexes of hydrogen-impurity and/or -defect. Hydrogen in Si and compound semiconductors, therefore, has been studied extensively in relation to device fabrication [8]. Hydrogen is also known to change the optical and electrical properties of various oxides. Interesting examples are coloration and bleaching of tungsten oxide [9–11] and change of resistivity of transparent conductors [12]. In niobium oxide hydrogen is reported to generate impurity donor levels in the band gap region [13].

Hydrogen in nitrides, however, has not been studied so extensively compared to other materials [14,15]. Hydrogen effects on GaN and InGaN films have been investigated in connection with the blue light emission diode and laser diode to avoid the acceptor passivation [16,17]. The stability of hydrogen in AlN and InN was confirmed as high as that in GaN, so the role of hydrogen in passivating dopants could be substantial in metallo-organic-based growth technique [14]. Thin films of InN prepared by RF ion-plating have been shown to reveal electrochromism, but interaction between hydrogen and InN has not yet been clarified [18]. Li_3N has attracted interest as a potential material for high energy density batteries because of lithium ionic conductivity [19,20]. When Li_3N was doped with hydrogen ions, it showed a higher ionic conductivity with low activation energy. This was explained in terms of the creation of lithium vacancies for charge compensation against nitrogen and hydrogen bonding [21].

The stoichiometric copper nitride (Cu_3N) has a unique crystal structure of anti-ReO_3 type. Maruyama and Morishita observed the change of Cu_3N from semiconductor to metal by adding extra copper atoms at the body center site of anti-ReO_3 lattice [22]. It can be considered that hydrogen occupies the hole site at the body center and affects the properties of the nitride.

Thin films of aluminum nitrides prepared by reactive sputtering show various electrical and optical properties depending on defects and non-stoichiometry of the compounds [23]. Hydrogen inclusion into the aluminum nitride films may be interesting in relation to the modification of the electronic properties of the compounds. The change of properties can be expected as reciprocal on charging and discharging of hydrogen.

We assume that hydrogen in metal nitrides may introduce hydrogen-related energy levels in the band gap as in

---

*Corresponding author. Tel.: +81-92-642-3679; fax: +81-92-632-0434.

E-mail address: hayashi@zaiko.kyushu-u.ac.jp (Y. Hayashi).

PII: S0925-8388(01)01495-5

metal oxides [13], and expect new properties in some nitrides which have not been paid much attention. In this study, thin films of nitrides with small and large band gap energies, Cu_3N and AlN, respectively, were prepared by RF reactive sputtering, and their electrical and optical properties were studied in relation to hydrogen inclusion. The modification of the electronic properties by hydrogen plays a role in developing a new material performance of thin films.

2. Experimental

Copper and aluminum nitride thin films were prepared by RF sputtering in a N_2 and Ar atmosphere using Cu and Al targets (99.9995%, 8 cm in diameter) and glass substrates. To obtain various films with different composition, nitrogen gas contents in Ar and N_2 mixture gas was controlled. Electrical resistivity and Hall effect were measured using the van der Pauw method at room temperature. Optical properties were measured with an optical spectrometer (Shimadzu UV-160A). Based on the measured transmittance and reflectance versus wavelength, the corresponding absorption coefficient, α, was calculated with the following equation:

$$T=[(1-R)^2\exp(-\alpha d)]/[1-R^2\exp(-2\alpha d)] \qquad (1)$$

where T is the transmittance, R is the reflectance, α is the absorption coefficient and d is the film thickness, which was about 500 nm.

Hydrogen was introduced by ion implantation at an acceleration voltage of 3 kV, and the dose was 1.6×10^{16} H_2^+/cm^2 for 1 h implantation. The implanted range meets nearly at the half depth of the films.

3. Experimental results and discussion

Copper nitride thin films with high resistivity were obtained with N_2 gas content higher than 20%. For more than 40% of N_2 the film structure was near stoichiometric Cu_3N.

The films prepared with low content of N_2 sputtering gas are composed of small particles of metal copper phase and Cu_3N semiconducting phase, and the overall resistance is governed by the semiconducting phase [24]. Copper nitride films prepared by various N_2 content in sputtering gas were examined. The resistivity decreased drastically by 1 h hydrogen implantation (1.6×10^{16} H_2^+ ions/cm^2) as shown in Fig. 1. The change of carrier concentration and Hall mobility were obtained as shown in Fig. 2. The carriers induced by hydrogen implantation were electrons. The larger influence of hydrogen implantation for specimens prepared with low N_2 content may be due to the presence of copper metal phase particles. The change of electrical resistivity and carrier density as a function of implantation time is shown in Fig. 3. They change quickly in the beginning of implantation and then gradually tend to

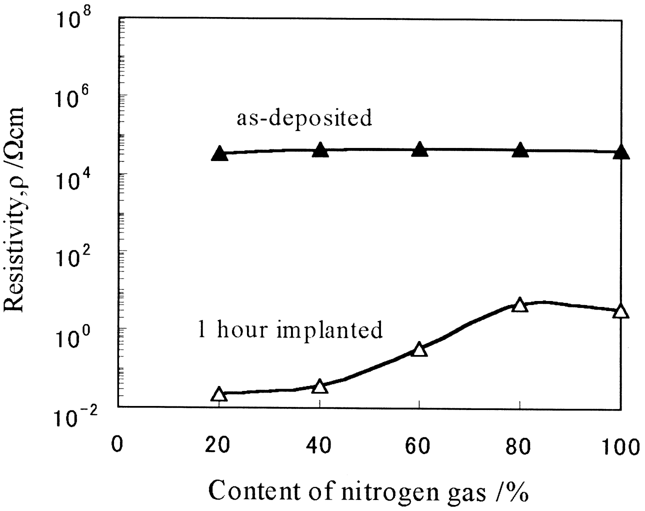

Fig. 1. Electrical resistivity of Cu–N thin films sputter deposited with changing the content of N_2 in sputtering gas. Change of resistivity by hydrogen implantation is shown. Hydrogen is implanted 1.6×10^{16} H_2^+ ions/cm^2 at 3 kV.

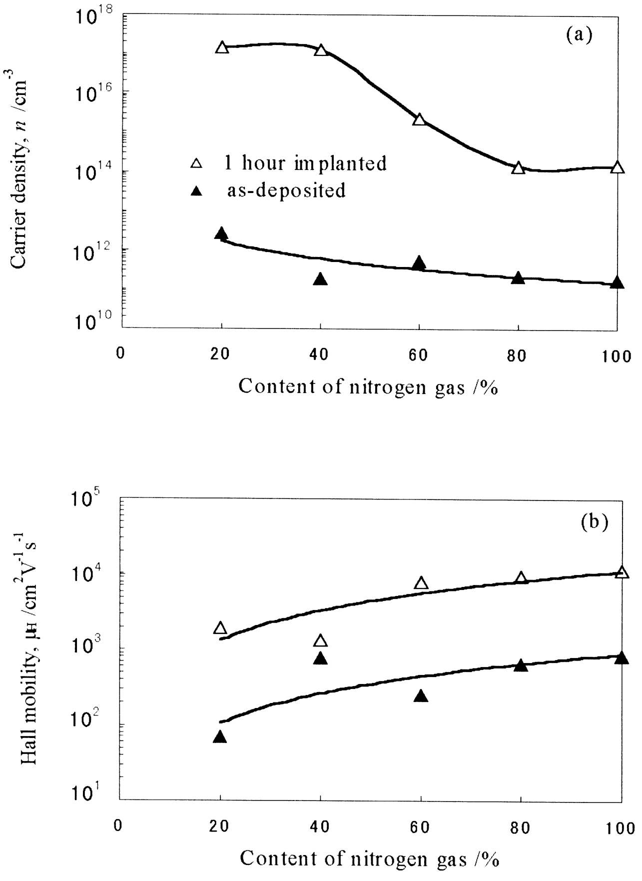

Fig. 2. Change of carrier density (a) and Hall mobility (b) by hydrogen implantation in sputter deposited Cu–N thin films prepared changing N_2 content in sputtering gas.

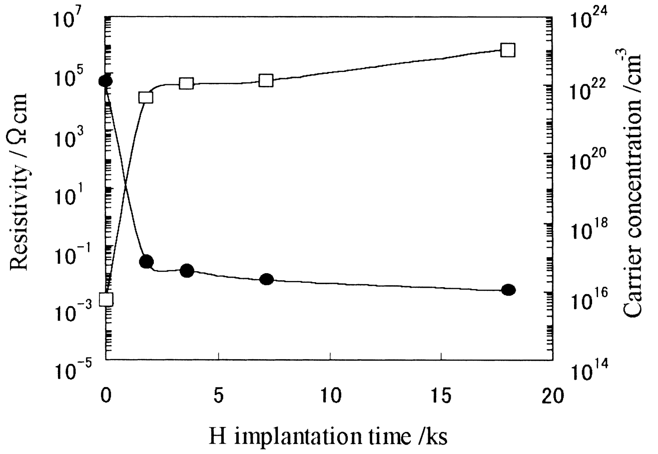

Fig. 3. Change of resistivity (●) and carrier density (□) by hydrogen implantation time for near-stoichiometric Cu_3N film. At 3.6 ks the dose is 1.6×10^{16} H_2^+ ions/cm^2.

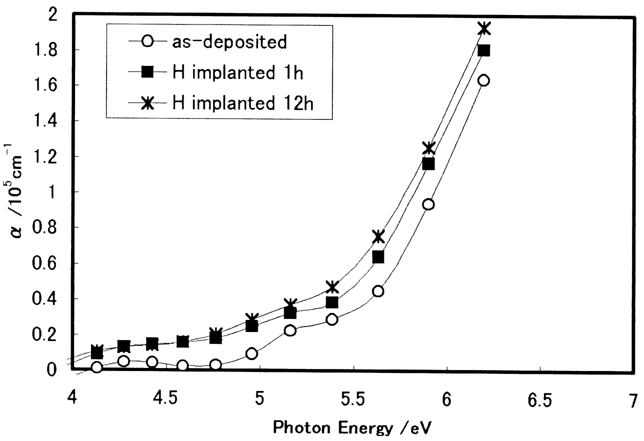

Fig. 5. Change of optical absorption coefficient a of AlN thin film by hydrogen implantation. At 1 h 1.6×10^{16} H_2^+ ions/cm^2 are implanted.

saturation. After hydrogen implantation for 5 h, the electrical resistivity of near stoichiometric Cu_3N was about 2.6×10^{-3} Ω cm and the carrier concentration was about 1.1×10^{23} cm^{-3}. There may be saturation for the inclusion of hydrogen and excess hydrogen may be released from the films.

The optical absorption coefficient α was calculated from the observed transmittance and reflectance. The optical transition type of Cu_3N is reported to be indirect [25]. The apparent band gap energy of the copper nitride specimens was, therefore, obtained by plotting $(\alpha h\nu)^{1/2}$ against photon energy ($h\nu$). An example of the change of absorption coefficient of near stoichiometric Cu_3N by hydrogen implantation is shown in Fig. 4. The absorption coefficient increased and band gap energy decreased by hydrogen implantation, but the change was easily recovered by evacuation anneal at 100°C.

If hydrogen deactivates defect states in the nitrides, electrical resistivity should increase. Since the carrier concentration was drastically increased with hydrogen implantation and the Hall coefficient was negative, hydrogen in copper nitrides would produce donor states rather than compensate defect states.

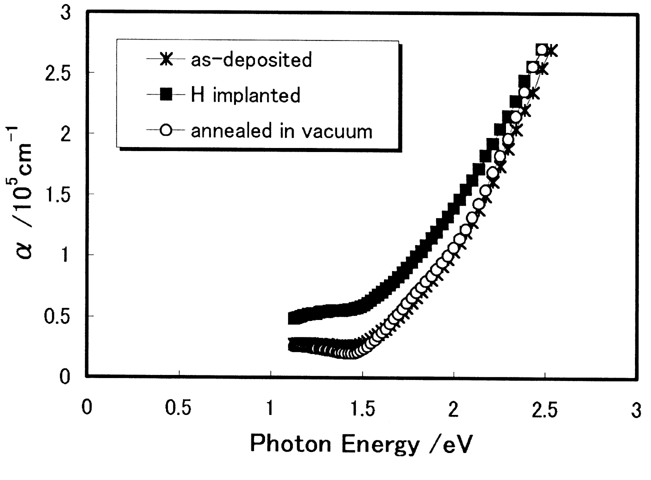

Fig. 4. Optical absorption coefficient a of near-stoichiometric Cu_3N. The spectrum changes by hydrogen implantation and evacuation anneal.

The thin films of near stoichiometric AlN had far too high resistivity to be measured by usual equipment. The spectrum of optical absorption coefficient is shown in Fig. 5. Change of the spectrum by hydrogen implantation is also shown in the figure. The optical absorption of AlN is reported to be a direct transition type [26], therefore the apparent band gap energy was obtained by plotting $(\alpha h\nu)^2$ against $h\nu$. By hydrogen implantation α increases as well as the band gap energy decreases. But the resistivity is still too high to be measured at room temperature. The nature of the modification by hydrogen is not so clear, but in the case of AlN also hydrogen may be considered to form impurity states in the band gap region.

Though the acceleration voltage was very low in ion implantation, formation of radiation damage may have some effect in electrical and optical properties. Consideration of the method of hydrogenation may be important for further study. Modification of electronic structure of nitrides may play a role in developing a new functional performance of materials.

4. Conclusion

Hydrogen effect on the electrical properties of near stoichiometric Cu_3N film was drastic; the electrical resistivity decreased with hydrogen implantation from 5×10^4 to 2.6×10^{-3} Ω cm, and carrier concentration increased from 6×10^{15} to 1.1×10^{23} cm^{-3}.

In AlN thin films the spectrum of optical absorption coefficient was modified by hydrogen implantation.

In copper and aluminum nitride films, modification of their electrical and optical properties by hydrogen inclusion may be mainly due to the formation of impurity donor states in the band gap energy. There are still interests in the interaction of hydrogen with structural defects in compounds for the development of a new functional performance of materials.

Acknowledgements

This work has been supported in part by a Grant-in-Aid for Scientific Research on Priority Areas A of 'New Protium Function' from the Ministry of Education, Science, Sports and Culture.

References

[1] J.N. Huiberts, R. Griessen, J.H. Rector, R.J. Wijngaarden, J.P. Dekker, D.G. de Groot, N.J. Koeman, Nature 380 (1996) 231.
[2] M. Kremens, N.J. Koeman, R. Griessen, P.H.L. Notten, R. Tolboom, P.J. Kelly, P.A. Duine, Phys. Rev. B 57 (1998) 4943.
[3] S.J. van der Molen, J.W.J. Kerssemakers, J.H. Rector, N.J. Koeman, B. Dam, R. Griessen, J. Appl. Phys. 86 (1999) 6107.
[4] E.S. Kooij, A.T.M. van Gogh, R. Griessen, J. Electrochem. Soc. 146 (8) (1999) 2990.
[5] G.G. Libowitz, Ber. Bunsenges. Phys. Chem. 77 (1973) 837.
[6] P. van der Sluis, M. Ouwerkerk, P.A. Duine, Appl. Phys. Lett. 70 (1997) 3356.
[7] D.G. Nagengast, A.T.M. van Gogh, E.S. Kooij, B. Dam, R. Griessen, Appl. Phys. Lett. 75 (1999) 2050.
[8] J. Pearton, J.W. Corbett, M. Stavola, in: Hydrogen in Crystalline Semiconductors, Springer, Berlin, Heidelberg, 1992.
[9] J.R. Platt, J. Chem. Phys. 34 (1961).
[10] S.K. Deb, Phil. Mag. 27 (1973) 801.
[11] B.W. Faughnan, R.S. Crandall, Display devices, Top. Appl. Phys. 40 (1980) 181.
[12] S. Kohiki, M. Nishitani, T. Wada, T. Hirano, Appl. Phys. Lett. 64 (21) (1994) 2876.
[13] Y. Hayashi, M. Arita, K. Koga, M. Masuda, J. Alloys Comp. 231 (1995) 702.
[14] J.M. Zavada, R.G. Wilson, C.R. Abernathy, S.J. Pearton, Appl. Phys. Lett. 64 (1994) 2724.
[15] T. Ishikawa, M. Masuda, Y. Hayashi, J. Jpn. Inst. Metals 47 (1999) 621.
[16] H. Amano, I. Akasaki, T. Kozawa, K. Hiramatsu, N. Sawaki, K. Ikeda, Y. Ishii, J. Luminesc. 40/41 (1988) 121.
[17] S. Nakamura, N. Iwasa, M. Senoh, T. Mukai, Jpn. J. Appl. Phys. 31 (1992) 1258–1266.
[18] N. Asai, Y. Inoue, H. Sugimura, O. Takai, Thin Solid Films 332 (1998) 267.
[19] B. A Boukamp, R.A. Huggins, Phys. Lett. 58A (1976) 231.
[20] U.V. Alpen, A. Rabenau, G.H. Talat, Appl. Phys. Lett. 30 (1976) 621.
[21] J. Wahl, Solid State Commun. 29 (1979) 485.
[22] T. Maruyama, T. Morishita, J. Appl. Phys. 78 (1995) 4104.
[23] D.Y. Wang, Y. Nagahata, M. Masuda, Y. Hayashi, J. Vac. Sci. Technol. A 14 (1996) 3092.
[24] D.Y. Wang, N. Nakamine, Y. Hayashi, J. Vac. Sci. Technol. A 16 (1998) 2084.
[25] T. Murayama, T. Morishita, J. Appl. Phys. 78 (6) (1995) 4104.
[26] X. Zhang, P. Kung, A. Saxler, D. Walker, T.C. Wang, R. Razeghi, Appl. Phys. Lett. 67 (12) (1995) 1745.