Inorganic Materials, Vol. 36, No. 11, 2000, pp. 1125–1126. Translated from Neorganicheskie Materialy, Vol. 36, No. 11, 2000, pp. 1340–1341.

Preparation of Ge_3N_4 Films on the Germanium Surface

I. G. Nakhutsrishvili, D. A. Dzhishiashvili, E. B. Miminoshvili, and M. A. Mushkudiani

Institute of Cybernetics, Academy of Sciences of Georgia, ul. Euli 5, Tbilisi, 380086 Georgia

Received March 19, 1999

Abstract—Single-phase β-Ge_3N_4 films free of GeO_2 and oxygen impurities were prepared on the surface of single-crystal germanium by nitriding with dry ammonia at 800°C.

To stabilize the electrical properties of germanium, a semiconductor as important as silicon and gallium arsenide, its surface must be protected with a layer of an oxygen-free compound. In view of this, the preparation of nitride films on the surface of single-crystal germanium has long been the subject of considerable attention (see, e.g.,[1, 2]).[1] The films produced on the germanium surface by nitriding typically comprise a dense nitride layer adjacent to the substrate and a loose nitride + GeO_2 layer. Occasionally, the films consist of a mixture of α- and β-Ge_3N_4. The purpose of this work was to obtain a single-phase, oxygen-free nitride film on germanium.

As substrates, we used *n*- or *p*-type (111) Ge wafers with a resistivity of 35–40 Ω cm, degreased in boiling toluene and chemically polished in the SR-4A etchant. The wafers were mounted in a cylindrical quartz reactor, which was then pumped down to ~1.3×10^{-2} Pa and filled with ammonia fed through a condenser trap. The reaction was run at a constant NH_3 pressure of ~1.33×10^3 Pa. The reaction products were characterized by Auger electron spectroscopy (AES) with an LAS-2000 spectrometer and x-ray diffraction (XRD) on an HZG-4A diffractometer (CuK_α radiation).

Below 800°C, no reaction products were detected on the Ge surface. At 800°C, a fairly thick (~0.3 μm), homogeneous dense film was produced in 2 h. Figure 1 displays the AES spectrum of this film after 30-min Ar^+-ion etching under conditions ($E_p \le 1$ keV, $I_p = 8 \times 10^{-7}$ A) sufficiently mild to avoid dissociation of the analyte. The spectrum contains only Ge and N peaks (the detection limit for oxygen is ~0.01 at. %). Thus, within the accuracy limits of Auger analysis, the film consists of only germanium and nitrogen. To check for the presence of excess Ge in the film, the AES spectrum was examined in detail between 1100 and 1200 eV. The strongest Ge peak, arising from the $L_3M_{4,5}M_{4,5}$ Auger transition, was found to be a singlet, indicating that no excess germanium was present. Note that the corresponding peak from a GeO_x two-phase film (GeO_2 + Ge) is split into two components separated by 7 eV [4].

The XRD pattern of the film in question (Fig. 2a) shows a strong Ge 111 peak and a few reflections from β-Ge_3N_4. By exposing Ge to dry ammonia at 800°C for 20 h, we obtained a film of nearly the same thickness, judging from the interference fringes. The XRD pattern of this film contained all of the main reflections from β-Ge_3N_4 (Fig. 2b); i.e., the film was fully crystallized. Note that, even at an increased counting time and anodic current and voltage, we did not detect reflections from Ge other than 111 or reflections from

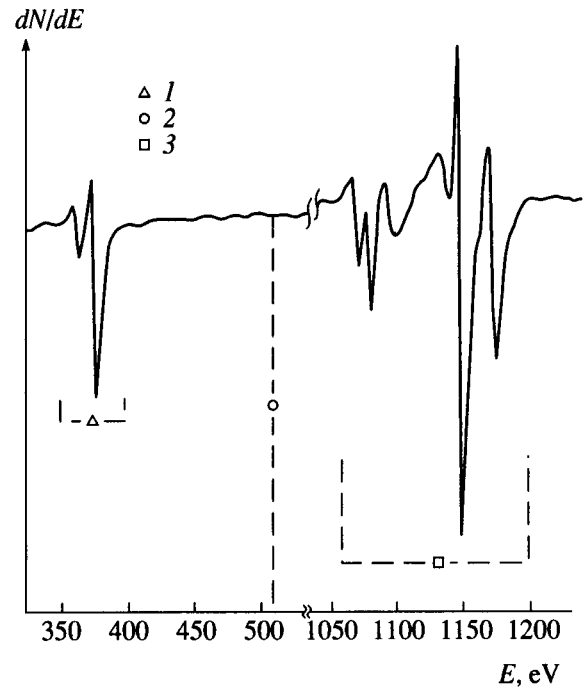

Fig. 1. AES spectrum of a germanium nitride film: (*1*) N, (*2*) O, (*3*) Ge.

[1] The only stable compound in the Ge–N system is Ge_3N_4, which can be prepared by nitriding elemental germanium in flowing ammonia by the reaction $3Ge + 4NH_3 \longrightarrow Ge_3N_4 + 6H_2$ [3]. Ge_3N_4 exists in two forms, α and β, both crystallizing in the hexagonal system with unit-cell parameters $a = 8.202$ Å, $c = 5.941$ Å for α-Ge_3N_4 and $a = 8.038$ Å, $c = 3.074$ Å for β-Ge_3N_4.

0020-1685/00/3611-1125$25.00 © 2000 MAIK "Nauka/Interperiodica"

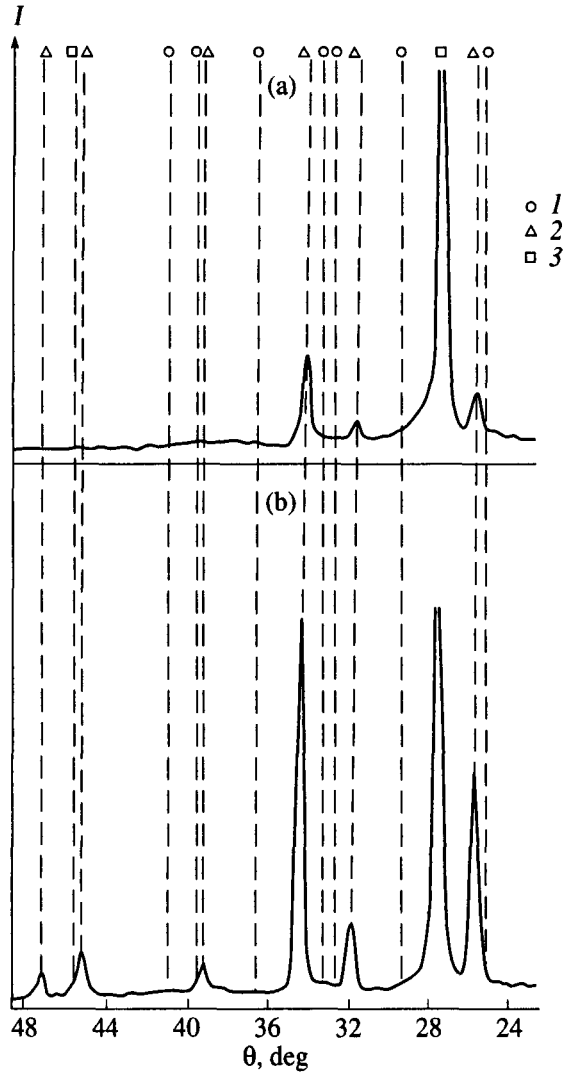

Fig. 2. XRD patterns from germanium nitride films prepared by exposing Ge to dry ammonia at 800°C for (a) 2 and (b) 20 h: (*1*) α-Ge_3N_4, (*2*) β-Ge_3N_4, (*3*) Ge.

α-Ge_3N_4. This, together with the AES data, suggests that the nitride film is single-phase and has a nearly stoichiometric composition.

Note also that we obtained identical AES and XRD data for the Ge_3N_4 films grown on *n*- and *p*-type Ge wafers, indicating that the presence of donor or acceptor impurities in Ge has no effect on the composition or structure of the film.

In electrical measurements, we used Ge/Ge_3N_4 samples with Al contacts. The flat-band voltage V_{FB} of these structures, characterizing the interfacial charge, was determined to be 1.2 V. The positive value of V_{FB} indicates that the interfacial layer is negatively charged on the film side. The interfacial charge density is low: $N_{FB} \sim 10^{11}$ cm^{-2}.

In conclusion, note that poling at 200°C for 5 min with a field of 2×10^6 V/cm changed V_{FB} by no more than 10%, indicating a high stability of the Ge/Ge_3N_4 interface.

ACKNOWLEDGMENTS

This work was supported by the Academy of Sciences of Georgia, grant no. 2.7.

REFERENCES

1. Hua, Q., Rosenberg, J., Ye, J., and Yang, E.S., Thin Germanium Nitride Films Grown by Thermal Reaction Process, *J. Appl. Phys.*, 1982, vol. 53, no. 12, pp. 8969–8973.
2. Synorov, V.F., Kuznetsova, E.A., and Aleinikov, N.M., Preparation of Nitrides on the Surface of Single-Crystal Germanium, *Izv. Vyssh. Uchebn. Zaved., Fiz.*, 1967, no. 3, pp. 7–11.
3. Samsonov, G.V., Kulik, O.P., and Polishchuk, V.S., *Poluchenie i metody analiza nitridov* (Preparation and Analysis of Nitrides), Kiev: Naukova Dumka, 1978, p. 187.
4. Bagratishvili, G.D., Nakhutsrishvili, I.G., Katsiashvili, M.R., and Dzhishiashvili, D.A., Phase Composition of Amorphous GeO_x Films, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1991, vol. 27, no. 6, pp. 1247–1250.