

From Eq. (10) we observe that as the voltage is ramped up, the condition for the current density at the source to be monotonically increasing (i.e., for  $dj(0, t)/dt$  not to change sign) is just

$$\frac{q^2}{2\epsilon_0 m} \left( \int_0^t j(0, t) d\tau \right)^2 - \epsilon_0 \frac{d^2}{dt^2} (qV) > 0. \quad (13)$$

Consequently, a loss in the monotonicity of the emitted current can only occur if  $qV(t)$  changes its inflection [i.e., if the second derivative of  $qV(t)$  changes sign]. If the voltage peaks earlier than the beam front transit time, a change in the inflection will always occur. A decrease in the emitted current will then depend on how the magnitude of the convexity of  $V(t)$  compares with the amount of charge in the diode region.

In conclusion, we have derived an equation which relates the space-charge-limited emission of current in a non-relativistic diode to the time-dependent applied voltage. The

equation is useful for identifying controls for time-dependent current emission. In a limiting case, we have obtained agreement with earlier calculations treating the beam dynamics associated with constant current emission.

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## Band-gap tailoring in amorphous germanium-nitrogen compounds

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In this letter some properties of off-stoichiometric amorphous germanium-nitrogen compounds are presented. It is shown that the inclusion of nitrogen atoms in the Ge network produces important changes in the optical and electrical properties of the material. The samples were prepared by rf sputtering a Ge target in an argon plus nitrogen atmosphere. Optical transmission and dark conductivity versus temperature measurements are presented and discussed. The preparation conditions permitted the variation of the optical band gap in a continuous way between 0.9 and 2.7 eV. As expected for unhydrogenated samples, the dark conductivity measurements indicate a high density of states in the pseudogap, confirmed by an ill-defined activation energy. Preparation conditions that might improve the transport properties are indicated.

Elemental and alloy amorphous semiconductor films have acquired increasing importance in the fields of microelectronics, image pick-up devices, and solar energy conversion. Depending on the preparation methods their properties can be varied by changing composition and/or deposition conditions. In particular *a*-Si based alloys obtained by the inclusion of column IV atoms and nitrogen have been extensively investigated. *a*-Si<sub>x</sub>C<sub>1-x</sub>:H (Ref. 1) and *a*-SiN<sub>x</sub>:H (Ref. 2) possess energy band gaps higher than *a*-Si:H, while *a*-Si<sub>x</sub>Ge<sub>1-x</sub>:H (Ref. 3) and *a*-Si<sub>x</sub>Sn<sub>1-x</sub>:H (Ref. 4) are narrower band-gap materials. At present, tailoring the optoelectronic properties of amorphous semiconductor alloys has been relatively successful. A lot of research work is being done, in particular with respect to transport properties that appear to be very sensitive to preparation conditions in a way that is not yet completely understood. In the field of photovoltaic conversion there is a need to find an active layer amorphous material having an energy band gap that opti-

mizes the electric power generation from the solar spectral distribution. This optimum band-gap value of 1.4–1.5 eV is easily obtained with *a*-Si<sub>x</sub>Ge<sub>1-x</sub>:H, *x* being in the 0.4–0.5 range. However, the inclusion of Ge atoms in the *a*-Si network deteriorates the transport properties of the alloy. Recent work shows that this effect depends on the preparation method and a much better material has been obtained by the glow discharge decomposition of GeF<sub>4</sub> + SiF<sub>4</sub> and H<sub>2</sub>.<sup>5</sup> At present it is not known if other amorphous germanium compounds will possess good photoelectronic properties.

An abundant literature exists on the properties of *a*-Ge (Ref. 6) and *a*-Ge:H (Ref. 7). Published reports describe methods for obtaining stoichiometric germanium nitride (Ge<sub>3</sub>N<sub>4</sub>) layers by reacting ammonia with germanium tetrahydrides or germanium, and by reacting germanium with hydrazine.<sup>8–12</sup> In Ref. 12 the properties of off-stoichiometric germanium oxynitride films as a function of oxygen content

TABLE I. Nitrogen relative partial pressures and extrapolated band gaps for some  $a\text{-GeN}_x$  samples ( $T_s = 360^\circ\text{C}$  and  $P_{N_2} + P_{Ar} = 1.2\text{ Pa}$ ).

Sample	03	06	07	08	09	10	11
$P_{N_2}$	0	$3 \times 10^{-3}$	$10^{-2}$	$3 \times 10^{-2}$	$10^{-1}$	$3 \times 10^{-1}$	$6 \times 10^{-1}$
$\frac{P_{N_2} + P_{Ar}}{E_g \text{ (eV)}}$	0.95	0.98	0.99	1.0	1.33	2.61	2.73

are described. Several reports exist also on the passivating properties of  $\text{Ge}_3\text{N}_4$  on GaAs and Ge surfaces.<sup>12-15</sup> Finally, the effect of nitrogen doping on  $c\text{-Ge}$  and  $a\text{-Ge}$  has been investigated by Pavlov *et al.*<sup>16</sup> and by Takano *et al.*<sup>17</sup>

To the present author's knowledge no reports exist on the fundamental properties of off-stoichiometric amorphous germanium nitride compounds. In this letter some determinations of these properties are presented. It is shown that, depending on the preparation conditions and nitrogen content in the Ge network, a variable band-gap material is obtained. The reported deposition conditions allowed us to continuously vary the forbidden band of  $a\text{-GeN}_x$  in the 0.9–2.73-eV range.

The samples were prepared by rf sputtering a Ge target in an argon plus nitrogen atmosphere in a Leybold-Heraeus Z-400 model system. The base vacuum was  $10^{-4}$  Pa and high-purity gases were used. For each series of samples all deposition conditions were kept constant, except the nitrogen partial pressure. The total gas pressure in the chamber and the substrate temperature were 1.2 Pa and  $360^\circ\text{C}$ , respectively. Nitrogen partial pressures were varied between  $4.5 \times 10^{-3}$  and 0.6 Pa. The sample thicknesses, determined by the deposition rate and by interference fringes, varied between 300 and 400 nm. Corning 7059 glasses were used as substrates in all cases. After deposition the structural properties were investigated by x-ray diffraction in a PW 1140 Philips generator ( $\text{CuK}\alpha$  line) coupled to a diffractometer at a scan speed of  $1\text{ deg min}^{-1}$ . All the samples, with exception of the one of pure Ge, proved to be amorphous by x-ray inspection. Optical measurements were made with a Beckmann DK 24 spectrophotometer. Dark conductivity as a function of temperature was measured in an evacuated chamber in the room-temperature –  $150^\circ\text{C}$  range. Coplanar 10-mm-long aluminium strips 0.5 mm apart were evaporated on the samples. Excellent ohmic behavior was observed in the 10–100-V polarization range. Conductivity measurements were performed within this bias range.

Table I indicates nitrogen partial pressures used in the preparation of some selected samples and the corresponding optical band gaps obtained by extrapolating the linear region of the  $(\alpha h\nu)^{1/2}$  vs  $h\nu$  plot to zero absorption ( $\alpha$  is the absorption coefficient).

X-ray diffraction measurements indicate a small degree of crystallinity for the pure Ge sample. Very small diffraction peaks appear coming from (111), (220), (311), and (400) planes. The position of the peaks, however, appears at angles  $0.2\text{--}0.3^\circ$  smaller than those corresponding to single crystal Ge. If minute flows of nitrogen are allowed in the chamber during deposition all signs of polycrystallinity disappear. The appearance of diffraction peaks when sputtering Ge at  $T_s \sim 360^\circ\text{C}$  is not at all surprising. Barna *et al.*<sup>18</sup> showed that

crystallization processes for evaporated Ge films begin in this temperature range. More recently Evangelisti *et al.*<sup>19</sup> investigated by extended x-ray absorption fine structure (EXAFS) the amorphous-to-crystal transition in thermal evaporated Ge films as a function of substrate temperature. They found that the structure of  $a\text{-Ge}$  evolves continuously to greater order as the deposition temperature increases in the interval from  $130$  to  $300^\circ\text{C}$  and no well-defined transition temperature can be defined. The absence of any x-ray structure in the films containing nitrogen was taken as a proof of amorphousness and later confirmed by Raman scattering measurements. This behavior might be interpreted by a lattice relaxation mechanism produced by the inclusion of nitrogen atoms with smaller coordination configurations. At present it is not known to what extent nitrogen atoms prefer to accommodate in a tetrahedral or a trigonal coordinated site in a Ge network. Nevertheless, some speculations can be made if the present material is compared to silicon-nitrogen compounds. It is useful to remember that  $\text{Ge}_3\text{N}_4$  crystallizes with the same structure as  $\text{Si}_3\text{N}_4$ . Chemical vapor and glow discharge deposited silicon nitride are amorphous. Radial distribution function experiments show that local configurations are very similar to those in stoichiometric polytype  $\beta\text{-Si}_3\text{N}_4$  with planar bonded N atoms and tetrahedral bonded Si.<sup>20</sup> This structure is consistent with  $sp^3$  silicon hybrid orbitals while N bonding is explained in terms of a linear combination of  $p$  orbitals, the planar geometry being given by a strong repulsion of nonbonded Si atoms.<sup>21</sup> Photoemission studies show that in  $a\text{-SiN}_x$  the valence-band maximum, dominated by Si  $3p$  states in  $a\text{-Si}$ , recedes linearly with  $x$  from 0 to 1.2. For  $x \geq 0.85$  the highest occupied states change over to N  $2p$ .<sup>22</sup> At the moment, no detailed calculations and measurements exist concerning  $a\text{-GeN}_x$ . Nevertheless, the similarities in the electronic valence structure of Si and Ge suggest that the coordination structure and the band-gap widening mechanism should not be very different in these materials.

Figure 1 shows a  $(\alpha h\nu)^{1/2}$  vs  $h\nu$  plot for some selected samples. It can be clearly seen that, as the nitrogen partial pressure in the reaction chamber increases, the extrapolated band gap widens in a continuous way. Within the experimental conditions reported here it was not possible to attain the stoichiometric composition of germanium nitride, whose

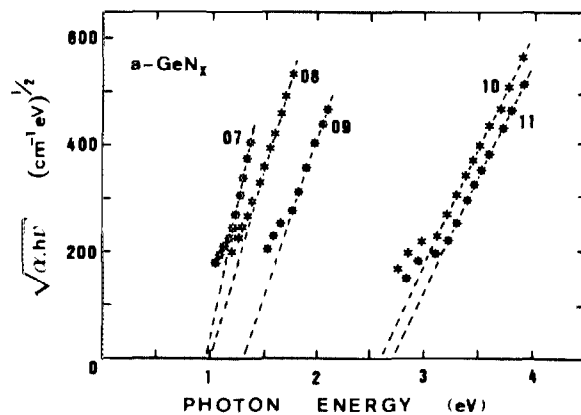


FIG. 1. Square root of the product of the absorption coefficient and the energy vs photon energy for some of the samples shown in Table I. Also the extrapolated optical band gaps are indicated.

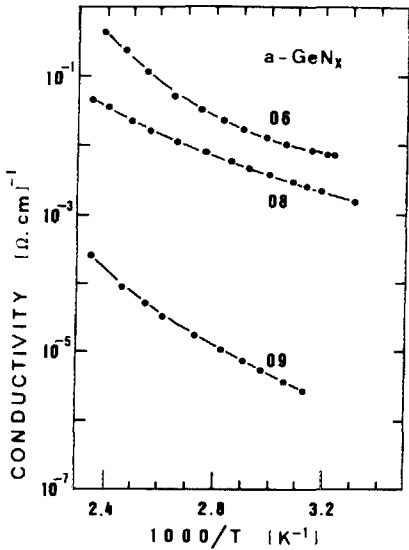


FIG. 2. Temperature dependence of the dark conductivity for some samples of Table I.

optical band gap has been reported to be higher than 4 eV.<sup>13,14</sup> In the series being discussed the maximum band gap was obtained when the nitrogen partial pressure was 0.6 Pa (i.e., equal to the Ar partial pressure). Figure 1 suggests that in  $a\text{-GeN}_x$ , as in the case of a  $a\text{-SiN}_x$ , threefold coordinated N becomes dominant over the fourfold coordinated N atoms for increasing  $x$ . The temperature dependence of the dark conductivity is shown in Fig. 2 for some selected samples. It can be seen that the resistivity of the samples increases as the nitrogen content increases, i.e., larger optical band gaps correspond to higher resistivities. A high density of defects in the pseudogap is expected and confirmed by an ill-defined activation energy. It is useful to remember that the samples are unhydrogenated.

The question concerning the use of hydrogen or fluorine to clean the pseudogap remains open. Experiments in that direction are being carried on. Other preparation methods may prove to be useful to produce an activated conductivity material, i.e., the glow discharge of  $\text{GeH}_4$  (or  $\text{GeF}_4$ ) +  $\text{NH}_3$ ,  $\text{GeH}_4$  (or  $\text{GeF}_4$ ) +  $\text{N}_2$  +  $\text{H}_2$ , etc.

In conclusion, it has been shown that as the nitrogen content increases in the Ge network a concomitant increase in the band gap of the material is observed. This observation suggests a kind of parallelism between the structural and bond characteristics of  $a\text{-GeN}_x$  and  $a\text{-SiN}_x$ .

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