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FIG. 3. Effective barrier height V_0 for a planar doped barrier structure vs half of the device length L at 300 K. Solid line = analytical solution [Eqs. (9a) and (9b)], dashed line = geometric model [Eq. (2)], dotted line in part (a) = analytical solution for a *n-i-n* structure ($Q_p = 0$), and $\epsilon = 1.14 \times 10^{-10}$ F/m, $N_d = 10^{25}$ m⁻³.

over from the n^+ regions is dominant and the barrier height is much closer to that for the *n-i-n* structure⁴ than to the value predicted by the geometrical model. At large values of Q_p and at 77 K the solution is more similar to that given by Eq. (2). However, the difference is still important because of the exponential dependence of the current through the structure on the barrier height.

The obtained results have important implications for the design of the planar doped barrier diodes¹ and transistors.² Equations (9) and (12) should be used in the design of these devices [instead of Eq. (2)] to account for the effects of the electron spill over on the barrier height.

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¹R. J. Malik, T. R. AuCorn, R. L. Ross, K. Board, C. E. C. Wood, and L. F. Eastman, Electron. Lett. **16**, 837 (1980).

²R. J. Malik, M. A. Hollis, L. F. Eastman, D. W. Woodard, C. E. C. Wood, and T. R. AuCorn, in *Proceedings of the Eighth Biennial IEEE Cornell Conference on High Speed Devices and Circuits*, August 1981, Ithaca, NY, pp. 87–96.

³R. F. Kazarinov and S. Luryi, Appl. Phys. Lett. 38, 810 (1981).

⁴A. van der Ziel, M. S. Shur, K. Lee, T. H. Chen, and K. Amberiadis, IEEE Trans. Electron Devices ED-30, 128 (1983).

n-MoSe₂/p-WSe₂ heterojunctions

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The preparation of n-MoSe₂/p-WSe₂ heterojunctions by epitaxial growth of WSe₂ ($E_g = 1.16 \text{ eV}$) on MoSe₂ ($E_g = 1.06 \text{ eV}$) substrates is reported. The two semiconductors are nearly lattice matched along their hexagonal (001) base plane with $\Delta a/a = 0.25\%$. Diode capacitance-voltage measurements show that the band edges of MoSe₂ and WSe₂ are aligned within $\sim 0.1 \text{ eV}$. The diode forward current at room temperature is carried by recombination in the depletion region.

We report a structure- and almost precisely latticematched heterojunction between two layered transition metal chalcogenide semiconductors. Both $MoSe_2$ and WSe_2 crystallize in the hexagonal MoS_2 -type structure. The lattice parameter *a* in the plane of the (001) layers is 3.288 Å for MoSe₂ and 3.280 Å for WSe₂; the parameter *c*, perpendicular to the plane, is 12.900 Å and 12.950 Å, respectively.¹ Thus the linear mismatch $\Delta a/a$ for the (001) interface is only

0.25%. The lowest energy band gaps are indirect for both semiconductors. They lie between 1.06 and 1.12 eV for $MoSe_2^{2.3}$ and between 1.16 and 1.22 eV for $WSe_2^{2.3}$ at room temperature. The energies of the lowest direct gaps have been reported as 1.35 eV for both $MoSe_2$ and $WSe_2^{.4}$

We prepared the $MoSe_2/WSe_2$ structures by epitaxial growth of p-WSe₂ layers on n-MoSe₂ substrate crystals.

The MoSe₂ single crystal substrates were grown from polycrystalline MoSe₂. The polycrystalline material was synthesized from molybdenum powder (99.99% wt.% pure) and selenium shot (99.999% wt. % pure). The elements were mixed, sealed in an ampoule of fused quartz, and heated to 600 °C for three days. The resulting MoSe₂ was remixed and again heated to 1000 °C for four days to ensure homogeneity. The single crystals were grown by vapor transport in sealed ampoules. MoSe₂ powder plus 15 mg of Se per cm³ of ampoule volume were distributed uniformly over 15-20 cm long ampoules. Se is the transport agent. The growth ampoule was encased in an outer ampoule. MoSe₂ crystals grew along the entire ampoule which was kept in a temperature gradient going from 1000 to 1070 °C. Within ten days, up to $100\,\mu\text{m}$ thick and 1–2 cm² large platelets formed. At 295 K a typical crystal had a resistivity of 2.5 Ω cm, a Hall mobility of 70 cm⁻² V⁻¹ s⁻¹, and a free-electron concentration of 3.5×10^{16} cm⁻³. These values are similar to others reported in the literature.5

High-purity polycrystalline WSe₂ was prepared and epitaxial WSe₂ films were grown as described earlier.⁶ For the growth of heterostructures in closed ampoules, MoSe₂ substrates were suspended from slots made in a fused quartz liner that was positioned in the colder half of the ampoule. The temperature along the ampoule ranged from 1060 at one



FIG. 1. Current-voltage characteristics of a $3.5 \text{ mm}^2 n$ -MoSe₂/p-WSe₂ heterodiode at six temperatures between 180 and 295 K. The indices denote the diode quality factor n.

end to 1070 °C at the other. The WSe₂ source powder and the Se transport agent were distributed uniformly along the ampoule. For a determination of the average film thickness the MoSe₂ substrates for two runs, of 38 and 90 h duration, were weighed before and after growth. Depending on the back-to-back or exposed positions of the MoSe₂ substrates, WSe₂ grew on one or on both sides. The weight increase was about 0.5 mg per hour and cm² substrate area, and proportional to the duration of growth. The WSe₂ film growth did not depend on the substrate position within the ampoule. The diodes incorporated 10–50- μ m-thick WSe₂ films.

The epitaxial structure of the WSe₂ overgrowth is immediately apparent from the orientation of steps and ledges of the WSe₂ films which are parallel to the edges of the characteristic raised or depressed hexagonal pyramids of the $MoSe_2$ substrate.

An 11- μ m-thick WSe₂ layer was cleaved off the epitaxial overgrowth for a determination of its electrical characteristics. The thermal voltage indicted *p*-type conduction. At room temperature the four-point resistivity was 8.3 Ω cm, the Hall mobility 270 cm⁻² V⁻¹ s⁻¹. The Hall mobility is typical for single crystals,⁷ but the net carrier concentration and conductivity of bulk crystals usually are 5 to 10 times higher than our values. It is not clear to which extent the low carrier concentration results from the growth process or from the cleaving.

For the fabrication of diodes, a $WSe_2/MOSe_2/WSe_2$ structure was first cleaved along a plane in the MoSe₂ substrate to expose the latter. Then 2–4 mm² pieces were isolated. These operations were carried out with a scalpel under a stereomicroscope. No chemical etch has yet been identified that could be used for the fabrication of mesa structures. A eutectic Ge-In alloy was employed as the contact metal to the *n*-type MoSe₂, silver paste to the *p*-type WSe₂, and Au lead wires for both. The diodes were characterized via their current-voltage (*I-V*) characteristics at 180–295 K, their room-temperature capacitance-voltage (*C-V*) characteristics at 1 kHz–1 MHz, and their photoresponse.

The diodes exhibit much better rectification than n-WSe₂/p-WSe₂ (Ref. 7) or n-ZrS₃/p-WSe₂ (Ref. 6). However, they are not ideal. At room temperature, the reverse leakage currents at 1 V lie between 10^{-6} and 10^{-5} A. The diode quality factor n ranges from 6 to 2.5 at around 200 K, to 2 at room temperature. Figure 1 displays the log I vs V charac-



FIG. 2. $1/C^2$ vs V characteristics of the diode of Fig. 1 at 1, 10, and 100 kHz.

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FIG. 3. Energy-band structure of the *n*-MoSe₂/*p*-WSe₂ heterojunction. MoSe₂: $N_D - N_A = 3.5 \times 10^{16}$ cm⁻³; WSe₂: $N_A - N_D = 4.4 \times 10^{15}$ cm⁻³.

teristics of one of our best diodes, for a range of temperatures. At 290 K, n = 2. This value reflects recombinationcontrolled carrier transport. As the temperature is lowered, *n* rises to 2.9 at 180 K, suggesting the transition to another mechanism which we have not identified. A plot of $\log I(V=0)$, extrapolated from the linear portions of the log I-V curves, vs 1/T results in activation energies ranging from 0.5 eV for the low-temperature points to 1 eV for high temperature. Because the forward conduction mechanism does change over the measured temperature range, these values cannot be considered reliable measures of the built-in voltage. The $1/C^2$ vs V characteristics for 1, 10, and 100 kHz are plotted in Fig. 2. The dispersion of the capacitance provides an indication for bulk and interface defects. With the 100 kHz data likely to be the least affected, we took these to obtain the density of ionized defects and the built-in voltage $V_{\rm bi} = 0.7$ V. Using relative dielectric constants in the $\langle 001 \rangle$ direction of 4.8 for $MoSe_2$ (Ref. 8) and of 4.2 for WSe_2 ,^{9,10} the width of the space charge at V = 0 is calculated at 0.29 μ m. The net acceptor density is 4.4×10^{15} cm⁻³. We assume that the p-WSe₂ is not compensated, and that the acceptors are fully ionized at room temperature. Then the density of ionized defects derived from the C-V measurement suggests that the junction space charge extends mainly, namely, 0.26 μ m, into the WSe₂ layer and only 0.03 μ m into the MoSe₂. We can construct the band diagram of the heterojunction after calculating the Fermi level positions E_F in the bulk of the two partners. The effective electron and hole masses m^* are assumed to be equal at the Γ point.^{11–13} Therefore, we set $m_e^*(MoSe_2) = m_h^*(WSe_2) = m_0$ (Ref. 14) and then use $N_c(MoSe_2) = N_v(WSe_2) = 2.54 \times 10^{19}$ cm⁻³ for the effective densities of states at 300 K. With $(E_c - E_F)$ for $MoSe_2 = 0.17$ eV and $(E_F - E_v)$ for $WSe_2 = 0.22$ eV and using $V_{bi} = 0.7$ V, we establish the band diagram of Fig. 3. We assume the band-gap energies of 1.06 eV for MoSe₂ and 1.16 eV for WSe_2 .² The built-in voltages are 0.07 V on the *n*-MoSe₂ side and 0.63 V on the *p*-WSe₂ side. The conductionband discontinuity at the interface, $E_c(WSe_2) - E_c(MoSe_2)$, is 0.07 eV and the valence-band discontinuity is -0.03 eV. In view of the identical crystal structure and the chemical similarity it is not surprising to see the band edges of $MoSe_2$ and WSe₂ almost exactly aligned.

When illuminated from the WSe_2 side with a tungstenhalogen lamp at about 100 mW cm⁻² this diode produced an open circuit voltage of 0.22 V.

The n-MoSe₂/p-WSe₂ diode characteristics clearly are superior to those of the n-ZrS₃/p-WSe₂ diodes reported earlier.⁶ This is a surprising result. It suggests that lattice match is necessary even across the van der Waals bonded interfaces of junctions between layered chalcogenides. However, the evidence cannot be considered definitive until means for diode fabrication can be found that will not require mechanical cutting which is likely to damage the semiconductor.

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- ²W. Kautek, H. Gerischer, and H. Tributsch, J. Electrochem. Soc. 127, 2471 (1980).
- ³K.-K. Kam, C.-L. Chang, and D. W. Lynch, J. Phys. C 17, 4031 (1984).
- ⁴K.-K. Kam and B. A. Parkinson, J. Phys. Chem. 86, 463 (1982).
- ⁵S. H. El-Mahalawy and B. L. Evans, Phys. Status Solidi B 79, 713 (1977).
- ⁶R. Späh, M. Lux-Steiner, E. Bucher, and S. Wagner, Appl. Phys. Lett. **45**, 744 (1984).
- ⁷R. Späh, U. Elrod, M. Lux-Steiner, E. Bucher, and S. Wagner, Appl. Phys. Lett. **43**, 79 (1983).
- ⁸A. R. Beal, W. Y. Liang, and H. P. Hughes, J. Phys. C 12, 881 (1979).
- ⁹A. R. Beal and W. Y. Liang, J. Phys. C 9, 2459 (1976).
- ¹⁰A. R. Beal, W. Y. Liang, and H. P. Hughes, J. Phys. C 9, 2449 (1976).
- ¹¹L. F. Mattheiss, Phys. Rev. B 8, 3719 (1973).
- ¹²D. W. Bullett, J. Phys. C 11, 4501 (1978).
- ¹³N. J. Doran, Physica B & C 99, 227 (1980).
- ¹⁴R. H. M. Fonville, W. Geertsma, and C. Haas, Phys. Status Solidi B 85, 621 (1978).

¹L. H. Brixner, J. Inorg. Nucl. Chem. 24, 257 (1962).