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Formation of anion vacancies by Langmuir evaporation from InP and GaAs (110) surfaces at low temperatures

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A low-temperature Langmuir-evaporation regime is observed by scanning tunneling microscopy on InP and GaAs (110) surfaces. It is characterized by the formation of positively charged anion monovacancies even at room temperature. This vacancy formation has been studied as a function of time on InP between 293 and 480 K and on GaAs at room temperature. On InP the maximum vacancy concentration is obtained at 435 K. At this temperature 1.2% of the P surface sites are vacant. At higher temperatures the concentration decreases. The observations are explained by a competition between, on the one hand, P-vacancy–adatom pair production followed by P_2 molecule formation and desorption and; on the other hand, phosphorus outdiffusion from the bulk.

I. INTRODUCTION

The surface of a compound semiconductor sample freshly cleaved in ultrahigh vacuum in general undergoes both structural and chemical changes. At elevated temperatures anions and cations evaporate freely from the surface. This nonequilibrium sublimation or Langmuir evaporation[1] has been studied on InP (Refs. 2–5) and GaAs (Refs. 6 and 7) surfaces. According to these investigations, two different temperature regimes can be defined: Up to the congruent evaporation temperature T_c anions (phosphorus or arsenic) and cations (indium or gallium) evaporate at equal rates. This temperature T_c ranges from 618 to 663 K in InP (Refs. 2 and 6) and from 905 to 950 K in GaAs,[6] depending on the orientation of the surface. Above T_c anions are preferentially lost, leading to the formation of cation clusters or droplets on the surface.

Until now studies of Langmuir evaporation have been primarily based on mass spectrometry. These studies were restricted to temperatures above about 575 K for InP and 800 K for GaAs. In the present paper we report on an application of scanning tunneling microscopy (STM) to the problem of Langmuir evaporation in compound semiconductors. We studied the temperature range between 293 and 480 K. We find a third evaporation regime at low temperatures, which is characterized by the formation of monovacancies in large concentrations. On InP and GaAs (110) surfaces thermal formation of phosphorus (P) and arsenic (As) vacancies already occurs at room temperature. On freshly cleaved surfaces the vacancy concentration increases with temperature up to a maximum of about 1.2% of the anion lattice sites at 435 K. At higher temperatures the concentration decreases again. These results are discussed in terms of anion evaporation and outdiffusion of anions from the bulk to the surface.

II. EXPERIMENT

The *p*-type InP and GaAs single crystals had a Zn dopant concentration of, respectively, $(1.3-2.1)\times10^{18}$ and 2×10^{17} cm^{-3}. Detailed high-sensitivity chemical analysis[8] of our InP material indicated a slight anion surplus, as it is usually the case in InP and GaAs single-crystal growth.[9] The samples were cleaved in ultrahigh vacuum to form reproducibility clean (110) surfaces. The InP samples were heated *ex situ* to a fixed temperature between 293 and 480 K at a pressure of 5×10^{-9} Pa. For each temperature a fresh surface was cleaved. The temperature was measured with a thermocouple pressed against the sample holder. The thermocouple signal was calibrated using the melting points of different indium alloys soldered on gold or silver pads sputtered on the crystals before cleavage. The temperature uncertainty is estimated to be ±10 K. After heat treatment at a given temperature for a given time, the samples were radiation cooled to room temperature within typically 30 min. Without breaking the vacuum the samples were then transferred to the scanning tunneling microscope. After microscopy the samples were reheated to the same temperature in order to study the time evolution of the surface defect concentration.

The P or As sublattice was imaged in the constant-current mode at a sample voltage of -2 to -2.8 V. We found that under these conditions no appreciable tip-induced defect production or defect migration occurred.[10–13]

III. EXPERIMENTAL RESULTS

Figure 1 shows the formation of defects on InP (110) at 435 K. After 5 min of heating, defects appear on the surface as dark spots. During further heating the density approaches a saturation value of about 5×10^{12} cm^{-2},

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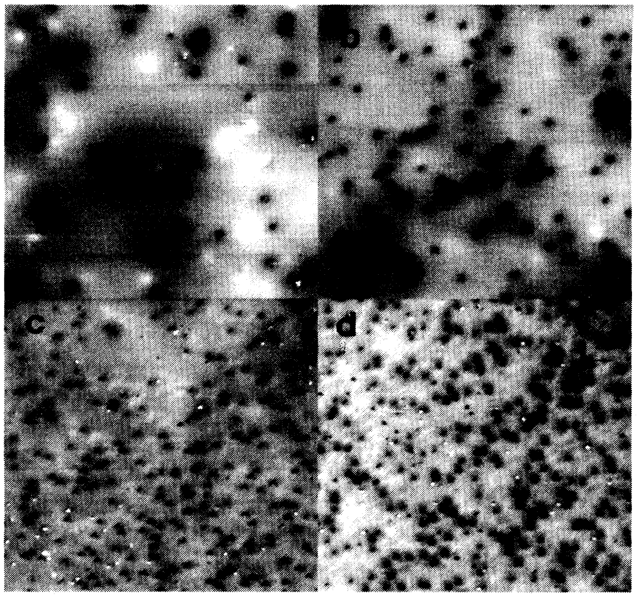

FIG. 1. STM images of the formation of P monovacancies during Langmuir evaporation of P from InP(110). The samples were heated at 435 K for (a) 5, (b) 65, (c) 443, and (d) 1253 min. The scan width is 75×75 nm^2 for each image.

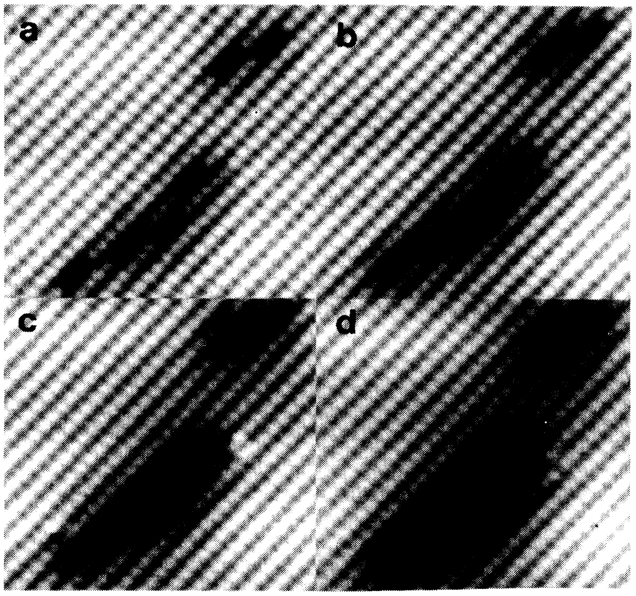

FIG. 2. The evaporation-induced defects in InP at atomic resolution. The P sublattice is shown at negative sample polarities of (a) -2.7, (b) -2.4, (c) -2.1, and (d) -1.8 V. The defects consist of one missing dangling bond and, as can be concluded from the voltage-dependent dark-contrast areas surrounding them, are positively charged. This indicates that the defects are phosphorus monovacancies.

which is reached after about 500 mins. The defects are shown in Fig. 2 at higher magnification. They each consist of one missing occupied dangling bond [Fig. 2(a)], which shows up as a geometric hole with a spatial extension of one atom (diameter about 0.4 nm). This hole is on average 0.07 nm deep. It can be observed at all negative voltages. In addition to this localized hole the defects are surrounded by a wide depression about 4–5 nm in diameter [Fig. 2(d)]. This depression is not a real deformation of the surface, but rather due to a reduction of the density of surface states induced by an electrostatic effect. The depth of the depression increases with decreasing negative tunneling voltages as shown in Fig. 2. This behavior is consistent with a local downward band bending induced by a positive charge of the defects.[10,14,15] In total our analyses of the electronic and geometric structures indicated that the defects are phosphorus monovacancies of the type observed earlier on *p*-doped InP (110) surfaces at room temperature.[16] As indicated by Fig. 2, there exists a minimum distance between vacancies and, for all temperatures and vacancy concentrations, we found essentially no divacancies or vacancy clusters. Neither did we observe indium vacancies, which we look for by inverting the tunneling voltage polarity.

At room temperature we occasionally observed bright points which we believe to be due to adatoms. In addition, we frequently observed scanning irregularities of the type expected when adatoms are touched and swept away by the tunneling tip. Such observations were, however, rare at the higher temperatures.

Figure 3 shows the P-vacancy concentration C_v on InP(110), defined as the fraction of anion sites vacant, versus heating time t at temperatures T between 293 and

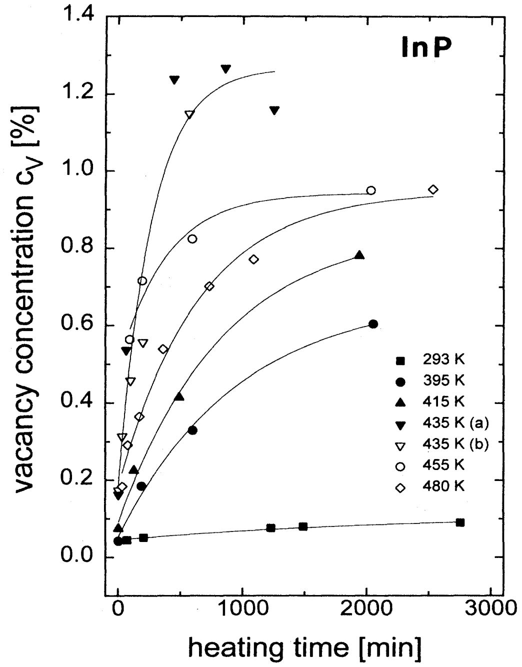

FIG. 3. Measured vacancy density on InP (110) C_v (fraction of empty P lattice sites) as a function of heating time t for different temperatures between 293 and 480 K. The measurement has been performed twice at 435 K to have an indication of the reproducibility. The lines serve only as guidance for the eye.

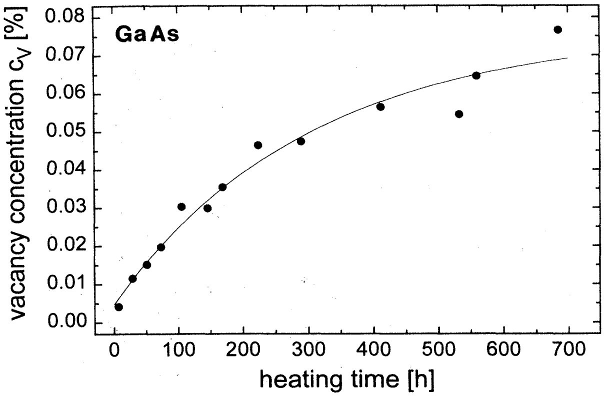

FIG. 4. Concentration of As monovacancies C_v formed during Langmuir evaporation of As from GaAs (110) at room temperature.

480 K. The concentrations were measured on the flat (110) surface at a sufficiently large distance from steps to exclude defect-denuded zones along them. The vacancy concentration immediately after cleaving at 293 K is about 2×10^{11} cm^{-2} or, with respect to the anion sublattice, 4.9×10^{-4} in atomic concentration. Up to 435 K the initial slope (formation rate) $(dC_v/dt)_i$ of the concentration increases with temperature. At higher temperatures it decreases again. We find that the vacancy concentrations approach a saturation value which increases with temperature up to 435 K. At higher temperatures it decreases again. If a sample is heated at 435 K to achieve the maximum vacancy concentration and subsequently heated at higher temperatures, a corresponding reduction of the vacancy concentration is observed.

Along the steps a vacancy-denuded zone occurs. Its width is of the order of magnitude of 10 nm and only weakly dependent on temperature. During heating, the steps themselves adopt an irregular shape and are frequently decorated by additional vacancies on their lower side.

Figure 4 shows the evolution of the defect concentration on the surface of a freshly cleaved GaAs (110) sample at room temperature. The analysis of the electronic and geometric structure indicates that the defects are positively charged arsenic monovacancies of the type observed earlier on GaAs (110) surfaces at room temperature.[17,18] The vacancy concentration immediately after cleaving is 4.5×10^{-5} per anion lattice site, and reaches 6.8×10^{-4} after 700 h.

IV. DISCUSSION

We observed the formation of phosphorus and arsenic surface vacancies at temperatures as low as room temperature on freshly cleaved (110) surfaces of, respectively, InP and GaAs. For the chosen scanning conditions, tip-induced vacancy formation can be excluded. The vacancy formation rate and the density after extended heating times depends systematically on temperature. From these observations we conclude that the observed vacancy formation is due to a thermal process which we attribute to Langmuir evaporation of phosphorus. The observation, on InP, of adatoms and frequent scanning irregularities at room temperature, but not at higher temperatures, may indicate that, at room temperature, an appreciable concentration of P adatoms resides on the surface, while at elevated temperatures rapid desorption occurs.

In the following discussion we concentrate first on the temperature range below 435 K. We assume that Langmuir evaporation of anions requires two steps, production of vacancy-adatom pairs followed by desorption of the adatoms. In principle, the energetically most favorable location for the formation of vacancy-adatom pairs is at kink sites of steps.[19] On the basis of simple geometrical arguments, in which any effect of defect-related bond relaxation is neglected, one finds that formation of an adatom by lifting an anion from its site on a flat (110) surface into an adatom position requires the breaking of three cation bonds. On the other hand, the formation of a vacancy at a kink site of a step extending along $[\bar{1}10]$ on a (110) surface requires the breaking of two bonds only, which is more favorable. From a kinetic point of view, however, this type of vacancy formation can only be continuous if stoichiometry is maintained. Thus continuous vacancy formation at steps requires the rate of cation-vacancy production at steps to be as high as that for the production of anion vacancies.

We believe, however, that vacancy formation at steps is not an efficient process in the temperature range investigated here. First of all, we can conclude, from the occurrence of a vacancy-denuded layer on both sides of steps, that steps do not act as sources for the vacancies observed on the terraces. Second, although quantitative observations of the atomic occupation right at the steps are difficult, we never observed In vacancies either in connection with steps or on the flat terraces. From this we conclude that In atoms are not removed from their lattice sites and thus are immobile. As a consequence, the contribution of steps to P evaporation should be very low since, after the initial desorption of the outermost row of P atoms, the steps are In terminated, which impedes any further P desorption. We therefore exclude a step-flow mechanism for the explanation of our observations.

Once thermal activation is sufficiently high to produce P adatoms on terraces, we can expect that the P adatoms are mobile because activation energy for surface diffusion should be lower than that for adatom formation. Diffusion can lead to adatom-vacancy recombination and to the formation of adatom clusters. Of these clusters we have to consider in particular the P_2 molecule, as it is generally accepted that phosphorus desorbs from InP in the form of such dimers.[2]

In the following we tentatively describe the nonequilibrium situation by a simple rate-equation treatment.[20] The rate equation includes the three processes discussed: the production and recombination of vacancy-adatom pairs and the formation of P_2 molecules. It is assumed that the dimer desorption is sufficiently rapid to keep the P_2 concentration so low that no additional rate terms have to be considered. Thus the rate at which the vacancy concentration C_v (fraction of empty anion sites) changes with time is given by

$$dC_v/dt = G(1 - ZC_v) - K_{av}C_aC_v \ , \tag{1}$$

where G is the thermal vacancy-adatom pair production rate, and Z is the number of sites around a vacancy on which, e.g., due to charge effects, an additional vacancy cannot be created. C_a is the adatom concentration (fraction of occupied anion sites in the virtual layer on top of the surface), and K_{av} is the reaction-rate coefficient for recombination. The corresponding rate for the adatoms is

$$dC_a/dt = G(1 - ZC_v) - K_{av}C_aC_v - K_{aa}C_a^2 \ , \tag{2}$$

where K_{aa} is the rate coefficient for P_2 molecule formation. The vacancy production rate can be written as

$$G = \nu_p \exp[-E_f/k_BT] \ , \tag{3}$$

where ν_p is an attempt frequency, E_f is an effective formation activation energy, and k_B denotes Boltzmann's constant.

First we discuss the following special cases.

(i) For short heating times and low vacancy concentrations C_v, Eq. (1) reduces to $dC_v/dt \approx G$. This means that the temperature dependence of the initial vacancy formation rate $(dC_v/dt)_i$ allows an estimate to be obtained for the effective vacancy formation energy using Eq. (1). At 293 K we obtain $(dC_v/dT)_i = (2.7 \pm 0.8) \times 10^{-7}\ \mathrm{s}^{-1}$ per anion lattice site from the data of Fig. 3. Since ν_p is not known, we tentatively assume that it is a Debye-type frequency in the range $10^9 \le \nu_p \le 10^{12}\ \mathrm{s}^{-1}$. Insertion into Eq. (3) yields $0.8 \le E_f \le 1.1$ eV for the effective vacancy-adatom pair formation energy. Employing this range of values in order to calculate, on the basis of Eq. (3), the defect production rates for the higher temperatures in Fig. 3, we find that the calculated rates for 395 K are between 100 and 3000 times greater than the experimentally observed one. From this we conclude that an additional process exists which strongly reduces the net vacancy production rate and its temperature dependence. As discussed below, this leads us to a consideration of the outdiffusion of phosphorus from the bulk.

(ii) If we take account of P_2 formation followed by rapid desorption, a maximum vacancy concentration is achieved when

$$C_v = 1/Z \ . \tag{4}$$

This means that the forbidden areas around existing vacancies overlap, allowing no further vacancy creation. Indeed, because the vacancies are electrically charged we expect a screened Coulomb repulsion between the vacancies, which can locally increase the effective vacancy-adatom pair formation energy and can possibly inhibit further vacancy production at higher concentration.

Our observation that a minimum distance exists between vacancies (Fig. 2), and that divacancies are essentially never observed, can be taken as evidence for these charge effects. However, we believe that the maximum concentration predicted by Eq. (4) has in fact not necessarily been reached in any of our experiments. A maximum vacancy concentration of above 1.2% was reached in the experiment at 435 K. Interpreting this concentration as corresponding to Eq. (4), we obtain a forbidden area of about 83 sites or 5 nm in diameter. This area corresponds roughly to the interaction range between the vacancies. On the other hand, there are still areas in Fig. 1 which are free of defects, especially for temperatures above 435 K. This observation leads us to the discussion of additional processes that impose a limit on the vacancy concentration before the value predicted by Eq. (4) is reached.

Although we have not yet investigated the temperature dependence of the Langmuir evaporation from GaAs (110), we have included our room-temperature results here (Fig. 4) in order to demonstrate the general nature of the reported phenomenon. Independent corroborative evidence for low-temperature anion vacancy formation on cleaved InP and GaAs surfaces is provided by a study by Mönch and Koenders[21] in which the temperature dependence of the work function was investigated using the Kelvin technique. They found an irreversible decrease in p-doped samples of InP (110) that they attributed to electrical states due to thermally induced surface vacancies. Similarly, Yamada and co-workers[22,23] performed photoemission experiments on InP and deduced the surface stoichiometry from the ratio of the P_{2p} and In_{4d} emission. During heat treatment at $300\ \mathrm{K} \le T \le 630$ K they observed that the surface became P deficient up to about 480 K. At the same time they observed a shift of the Fermi level into the gap. At $T > 480$ K the surface began to recover its normal stoichiometry, which was reached at 630 K. Because of the associated Fermi-level shift the authors attributed their observations, on the basis of theoretical work by Dow and Allen,[24] to selective P evaporation accompanied by anion-vacancy formation, since the latter should have the character of donors. Our results demonstrate that indeed positively charged P vacancies are created.

We have seen that our results cannot be explained on the basis of Eqs. (1) and (2) without further assumptions. In addition, detailed analysis of these equations and their rate coefficients indicates that it is not possible to explain any decrease of the vacancy production rate or maximum vacancy concentration with increasing temperature above 435 K without including in Eqs. (1) and (2) a further process. The following experiments provide some indications about this process.

Massies and Lemaire-Dezaly[25] observed, by Auger and electron-energy-loss spectroscopy, that on InP surfaces the P/In ratio increased upon cooling from 450 to about 350 K. They attributed this increase to a competition between outdiffusion from the bulk and preferential loss of P from the surface. Furthermore, Bartels, Clemens, and Mönch reported[26] that on freshly cleaved GaAs (110) surfaces an increased arsenic concentration could be detected by Auger-electron and low-energy electron-energy-loss spectroscopy after the samples had been kept in ultrahigh vacuum at room temperature for about 24 h. From this they concluded As outdiffusion from the bulk.

On the basis of these results we explain our observations by the combined effect of two processes, Langmuir evaporation from the surface and outdiffusion of phosphorus from the bulk. In order to account for the reduced temperature dependence [compared to the prediction of Eq. (3)] of the initial vacancy formation rate $(dC_v/dt)_i$ and the decrease of the maximum vacancy concentration above 435 K, the relative effect of P outdiffusion has to increase with temperature. This requires that the effective activation energy for outdiffusion is somewhat greater than that for surface vacancy formation.

It is difficult to compare our results with literature data on the P diffusion in InP crystals because the literature data themselves are contradictory:[27] Radioactive tracer experiments on bulk InP yielded an activation energy of 5.65 eV for P diffusion excluding substitutional P from playing any role in the temperature range investigated in our experiments.[28] On the other hand, from the results of emission channeling[29] and electron paramagnetic resonance experiments,[30] it was concluded that vacancies become mobile below 400 K and, in radiation damage experiments, free interstitial P mobility was observed just above room temperature.[27]

Another reason why a comparison with our measurements difficult is the fact that the available diffusion data concern only bulk diffusion. It is conceivable that bulk diffusion energies are significantly different from near-surface area diffusion energies or from cases where, as here, the surface composition tends to deviate from that in the bulk. Nevertheless, this nonstoichiometry of the surface may, at least to a certain extent, be compensated for by outdiffusion from the bulk. Indeed, vacancy migration into the bulk was concluded from the results of a study of high-temperature Langmuir evaporation on CdTe.[31] Another possibility is that in our sample the excess of P does not occupy substitutional but interstitial sites. In this case it is conceivable that outdiffusion occurs via an interstitialcy mechanism with a lower activation energy than for the vacancy mechanism. However, at the present stage it is difficult to provide a definitive conclusion about the atomistic mechanism of phosphorus outdiffusion.

V. SUMMARY

By scanning tunneling microscopy we observed a low-temperature Langmuir evaporation regime from the InP and GaAs (110) surfaces. It is characterized by the formation of positively charged anion monovacancies in large concentrations. This vacancy formation has been studied quantitatively on InP (110) surfaces between 293 and 480 K and on GaAs (110) surfaces at room temperature. The presence of P monovacancies suggests that the desorption process occurs via a vacancy-adatom pair production as a first step, which is followed by the formation of P_2 molecules that then escape from the surface. No evidence was found for corresponding In evaporation. The maximum vacancy concentration is obtained at 435 K, where 1.2% of the P surface sites are vacant. At higher temperatures the P-vacancy concentration decreases again with increasing temperature. This is explained by phosphorus outdiffusion from the bulk.

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[1] W. Mönch, *Semiconductor Surfaces and Interfaces* (Springer-Verlag, Berlin, 1993).

[2] R. F. C. Farrow, J. Phys. D **7**, 2436 (1974).

[3] W. Y. Lum and A. R. Clawson, J. Appl. Phys. **50**, 5296 (1979).

[4] P. K. Gallagher and S. N. G. Chu, J. Phys. Chem. **86**, 3246 (1982).

[5] L. G. van Uitert, P. K. Gallagher, S. Singh, and G. J. Zydzik, J. Vac. Sci. Technol. B **1**, 825 (1983).

[6] B. Goldstein, D. J. Szostak, and V. S. Ban, Surf. Sci. **57**, 733 (1976).

[7] C. T. Foxon, J. A. Harvey, and B. A. Joyce, J. Phys. Chem. Solids **34**, 1693 (1973).

[8] G. Wolff and A. Holthenreich (unpublished).

[9] H. Wenzl, W. A. Oates, and K. Mika, in *Thermodynamics and Kinetics,* edited by D. T. J. Hurle, Handbook of Crystal Growth Vol. 1A (North-Holland, Amsterdam, 1993), p. 103.

[10] Ph. Ebert and K. Urban, Ultramicroscopy **49**, 344 (1993).

[11] Ph. Ebert and K. Urban, Surf. Sci. **287-288**, 891 (1993).

[12] Ph. Ebert, M. G. Lagally, and K. Urban, Phys. Rev. Lett. **70**, 1437 (1993).

[13] S. Gwo, A. R. Smith, and C. K. Shih, J. Vac. Sci. Technol. A **11**, 1644 (1993).

[14] J. A. Stroscio, R. M. Feenstra, and A. P. Fein, Phys. Rev. Lett. **58**, 1668 (1987).

[15] R. J. Hamers, J. Vac. Sci. Technol. B **6**, 1462 (1988).

[16] Ph. Ebert, K. Urban, and M. G. Lagally, Phys. Rev. Lett. **72**, 840 (1994).

[17] G. Lengel, R. Wilkins, G. Brown, M. Weimer, J. Gryko, and R. E. Allen, Phys. Rev. Lett. **72**, 836 (1994).

[18] G. Cox, Ph. Ebert, and K. Urban, Inst. Phys. Conf. Ser. **117**, 347 (1991).

[19] T. Y. Tan, Mater. Sci. Eng. B **10**, 227 (1991).

[20] J. Philibert, *Atom Movements, Diffusion, and Mass Transport in Solids* (Les Edition de Physique, Les Ulis, 1991).

[21] W. Mönch and L. Koenders, in *Proceedings of the 17th International Conference on the Physics of Semiconductors,* edited by J. D. Chadi and W. A. Harrison (Springer Verlag, New York, 1985), p. 85.

[22] M. Yamada, A. K. Wahi, P. L. Meissner, A. Herrera-Gomez, T. Kendelewicz, and W. E. Spicer, Appl. Phys. Lett. **58**, 2243 (1991).

[23] M. Yamada, A. M. Green, A. Herrera-Gomez, T. Kendelewicz, and W. E. Spicer, Jpn. J. Appl. Phys. Lett. **30**, L1982 (1991).

[24] J. D. Dow and R. E. Allen, J. Vac. Sci. Technol. **20**, 659 (1982).

[25]J. Massies and F. Lemaire-Dezaly, J. Appl. Phys. **57**, 237 (1985).

[26]F. Bartels, H. J. Clemens, and W. Mönch, Physica **117B&118B**, 801 (1983).

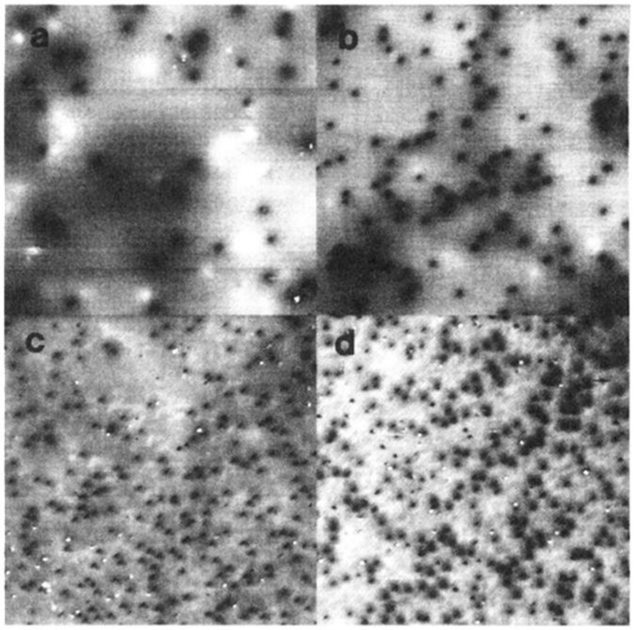
[27]K. Karsten (unpublished).

[28]B. Goldstein, Phys. Rev. **121**, 1305 (1961).

[29]U. Wahl, H. Hofsäss, S. G. Jahn, S. Winter, and E. Recknagel, Nucl. Instrum. Methods Phys. Res. B **64**, 221 (1992).

[30]H. J. Bardeleben, Solid State Commun. **57**, 137 (1986).

[31]P. Juza, W. Faschinger, K. Hingerl, and H. Sitter, Semicond. Sci. Technol. **5**, 191 (1990).



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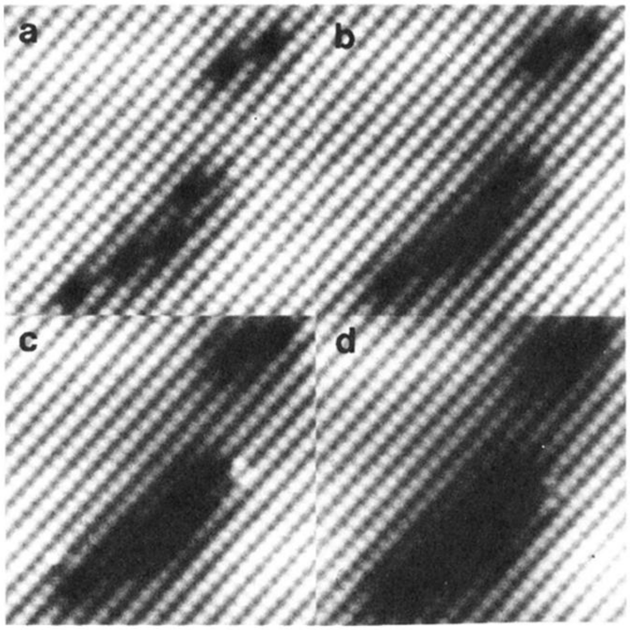

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