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GaAs wafer bonding by atomic hydrogen surface cleaning

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A method of large-area wafer bonding of GaAs is proposed. The bonding procedure was carried out in an ultrahigh vacuum. The wafer surfaces were cleaned at 400 and 500 °C by application of atomic hydrogen produced by thermal cracking. The wafers were brought into contact either immediately after the cleaning, or at temperatures as low as 150 °C, without application of a load, and successfully bonded over the whole area. High-resolution transmission electron microscopy revealed that the wafers could be directly bonded without any crystalline damage or intermediate layer. From a mechanical test, the fracture surface energy was estimated to be 0.7–1.0 J/m^2, which is comparable to that of the bulk fracture. Furthermore, this bonding method needs no wet chemical treatment and has no limits to wafer diameter. Moreover, it is suitable for low temperature bonding.
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I. INTRODUCTION

Gallium arsenide is a III–V compound semiconductor material of the most importance in opto- and high-speed electronics. The ability to join two GaAs wafers with each other or with other materials would represent an additional degree of freedom in the design of opto-electronic systems and enhance the flexibility of fabrication procedures. Because ''wafer direct bonding'' [1] does not depend on a third material acting as a glue, it may be seen as the joining technique of choice. So far, direct bonding of GaAs has often been carried out in inert or reducing atmospheres, at relatively high temperatures between 400 and 975 °C for a few up to 20 h, often under a compressive load of up to 40 kg/cm^2, and for small pieces of approximately 1 cm^2 area.[2–4]

The postbonding high-temperature annealing is intended to increase the adhesion between the sample, and to remove any enclosed surface adsorbates. This approach, however, often compromises the quality of the interface and of the bonded materials: interlayers of gallium or arsenic oxides may be enclosed or bubbles may form because of thermal decomposition of surfaces adsorbates. Moreover, the high annealing temperatures are not adequate for bonding dissimilar materials due to mismatches in thermal expansion behavior. In addition, the application of a mechanical load easily induces structural damage and is particularly difficult to extend to whole wafers. Large-area wafer bonding[5] is, however, a necessity for virtually all practical applications.

Therefore, more moderate bonding conditions are necessary, which would enable bonding at lower temperatures and without applied pressures. In fact, in the case of wafer bonding of Si, it was shown that, if atomically clean surfaces are prepared, the covalent bonding can occur even at room temperature.[6,7] A H-terminated Si wafer pair was heated to desorb the hydrogen, and thus to obtain the clean Si surface. As long as this clean surface can be maintained, e.g., in an UHV, the wafers can be brought into contact to bond at any desired temperature, even down to room temperature. In this case, practically no pressure was applied to bond whole 4 in. wafers by forming an atomically abrupt interface. Alternatively, an ion beam was applied for surface cleaning and activation, to bond not only Si but also dissimilar III–V compounds without any heating process,[8,9] but this procedure can involve some ion beam damage left at the bond interface.

Thus, the preparation of a clean and damage-free wafer surface was considered to be inevitable to achieve our purpose. The cleaning procedure of GaAs surfaces is more complex than that of Si, due to the difficulty in removing the oxide of Ga and As congruently. GaAs surfaces exposed to air consist of native oxides, carbon contaminants, and absorbed water. Water can be thermally removed at relatively low temperatures. Then native oxides are desorbed by heating up to 580 °C. However, it has been reported that thermal cleaning cannot remove carbon contaminants completely[10] and leads to surface roughness[11,12] and accumulation of impurities,[13,14] even if the oxide layer can be removed.

As a cleaning method, electron cyclotron resonance (ECR) plasma has been reported to be effective.[15–18] It is actually atomic hydrogen in ECR plasma that has the cleaning effect. Atomic hydrogen, or hydrogen radical (H·), can effectively be generated by thermal decomposition of molecular hydrogen flowing through a hot tube.[19] It was found out that the thermally generated atomic hydrogen causes less damage due to the less momentum of the formed H·, the cleaning mechanism has been studied in detail.[20–26]

The cleaning process may be summarized as follows: Arsenic oxide desorbs easily by heating. As a result, the surface becomes Ga rich. Therefore, the role of the atomic hydrogen is to remove not only the arsenic oxide but also the nonvolatile gallium oxide, Ga_2O_3, which would otherwise remain. Arsenic oxides can be removed not only by heating but also by H· cleaning

$$As_2O_x + 2x\mathrm{H}\cdot \rightarrow x H_2O\uparrow + As_2(\tfrac{1}{2}As_4)\uparrow,$$

where $x = 1$, 3, or 5 stands for the various oxides of arsenic. Ga_2O_3 is decomposed as

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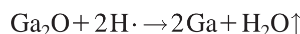
TABLE I. Cleaning and bonding conditions.

Condition	Hydrogen species	Cleaning temperature (°C)	Time (min)	Bonding temperature (°C)
(I)	H·	400	30	
		500	30	~400
(II)	H·	400	30	
		500	30	150
(III)	H·	400	30	150
(IV)	H_2	400	30	~350 (notbonded)
(V)	Without hydrogen	400	30	~350 (notbonded)

$$Ga_2O_3 + 4H\cdot \rightarrow Ga_2O(\uparrow) + 2H_2O\uparrow.$$

Ga_2O becomes volatile at temperatures higher than ~200 °C. Accordingly, exposure to H· at temperatures below 200 °C does not remove the Ga_2O surface layer, which then functions as an etch stop, or leads to a Ga-rich surface by the reaction



$$Ga_2O + 2H\cdot \rightarrow 2Ga + H_2O\uparrow$$

which is harmful for device applications. Therefore, the temperature should be chosen not below 350 °C, preferably higher than 400 °C, so that Ga_2O desorbs reliably. It has been shown that C–O molecules can also be removed.[23]

Thus, native oxides can be removed, and a clean stoichiometric GaAs surface can be obtained. Once these surfaces are brought into contact, they should form covalent bonds directly. This article is a report of successful direct large-area wafer bonding of GaAs at relatively low temperatures. The procedure requires no applied pressure and preserves the crystallinity of the bonded wafer materials.

II. EXPERIMENT

2 and 3 in. liquid encapsulated czochralski grown semi-insulating GaAs (001) wafers with ''epi-ready'' surface quality produced by Freiberger Compound Materials GmbH were used. As a protective first step, immediately after unpacking the wafers in a cleanroom, they were put together face-to-face to reversibly bond them.[27] The purpose of this step is to avoid particle invasion during the handling in air until setting into the UHV system. No wet chemical cleaning was done at all. The wafer pair was inserted vertically into the UHV system of a background pressure of less than 5×10^{-11} Torr, and was separated by ~ 1.5 cm using sharp blades. Then the wafers were heated from both sides first up to 400 °C. After confirming the decrease of water and contaminants desorbing from the wafers by a mass spectrometer, typically after 10–15 min, an atomic hydrogen beam was applied into the opening between the two wafers at certain temperatures as mentioned later (also see Table I).

The atomic hydrogen beam is produced by feeding hydrogen gas through a tantalum capillary heated by electron bombardment to 2100 K.[28–30] The temperature of the capillary was measured by a pyrometer. During the cleaning process, the hydrogen flow rate was controlled so that the pressure of the atmosphere was maintained at 1.0×10^{-6} Torr. Here, the decomposition efficiency of hydrogen was not measured, but a similar system was investigated in detail in Refs. 29 and 30.

The cleaning and bonding conditions are listed in Table I. The wafer surface was cleaned for 30 min at 400 °C first and for the next 30 min at 500 °C (I and II) or only for 30 min at 400 °C (III). For condition (I), the wafers were brought into contact immediately, typically within 1 min, after the surface cleaning, whereas, for (II) and (III), the bonding was performed after the temperature decreased below 150 °C, i.e., after ~ 15 min. The wafers were then gently brought into contact by rods from both sides. Before bonding, the [110] directions of the both wafers were aligned parallel by using the orientation flats of the wafers. Therefore, the orientational accuracy was within ±1.0° from the error in crystallographic orientation of the wafer flats. No intentional load was applied larger than that just enough for the wafers to move until they touch each other. For comparison, heat treatments were performed at 400 °C under two more conditions: (IV) H_2 atmosphere with the same total pressure of 1.0×10^{-6} Torr for 30 min, and (V) in UHV without introduction of H_2.

The interfaces were analyzed by infrared transmission pictures, double cantilever beam (DCB) tests, and transmission electron microscopy (TEM) (JEOL 4000EX and Philips CM20T). TEM samples were taken from the central part of the bonded areas.

III. RESULTS AND DISCUSSION

A. Large-area bonding

Figures 1(a) and 1(b) show typical *in situ* infrared pictures taken before separating the prebonded wafers (a) and after UHV bonding, following the H· surface cleaning (b). In all the cases where this bonding was successful, the wafers bonded to each other so fast almost all over the wafer area that the progress of the bonding front could not be followed using an infrared camera. The first contact point of the wafers should be either at the center where rods touched to initiate the contact or somewhere at the edge of the wafer. In either case, the bonding spontaneously spreads from the contact point over the wafer area. Even though the wafers were gently pressed at the initiating point, the vast majority of the wafer area was bonded without any load. Therefore, it can be concluded that the wafers can be bonded practically with no load applied. In addition, the bonding was successfully performed all over the wafer to the wafer edge. Before separating the wafer pair which had been weakly prebonded for protection, at least three voids could be seen [Fig. 1(a)]. The origin of the voids may be attributed to particles on the wafer surface. After UHV bonding, two of the three disappeared; no other macroscopic defects were found.

The ''bond energy'' was measured by the DCB test, where the fracture surface energy was calculated from the crack length at each point as the blade is gradually inserted into the interface plane (Fig. 2). The fracture surface energy, γ, was calculated using the formula

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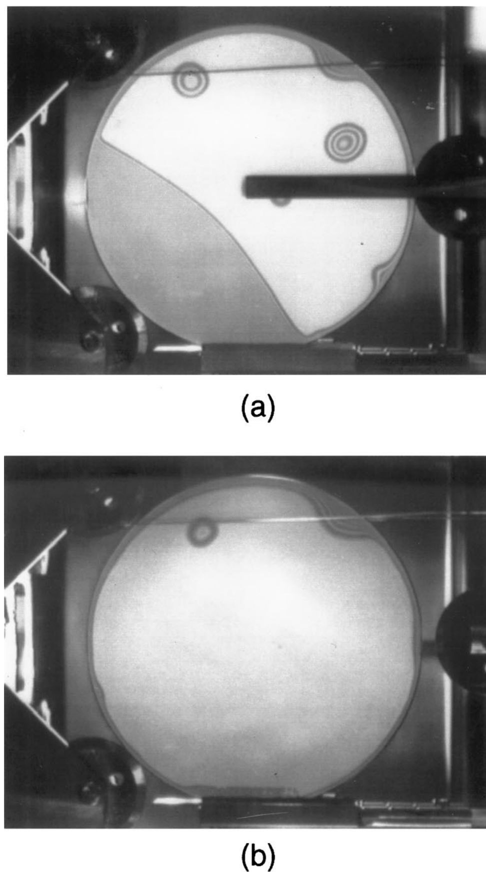

FIG. 1. Infrared transmission pictures of 3 in. wafer pair (a) before opening and (b) after bonding.

$$\gamma = \frac{3Et_w^3 t_b^2}{32L^4}, \tag{1}$$

where E is Young's modulus of GaAs, t_w the wafer thickness, t_b the thickness of the blade, and L the crack length at each blade insertion position. Figure 2 shows the results of cases II and III. The fracture surface energy was estimated to be 0.7–1.0 J/m^2 which is comparable to that of the bulk, 0.9 J/m^2.[31] The results for the case II incidate an error of ~ 0.2 J/m^2. A strong bond energy was obtained even for the case of III. Thus, hydrogen cleaning guarantees strong chemical bonds at the interface, sufficient for any application.

Bonding conditions IV (annealing in molecular hydrogen) and V (*in vacuo* annealing) unambiguously demonstrate the importance of atomic hydrogen: Neither treatment (IV) nor (V) attained covalent bonding. In fact, after either treatment the wafers did not adhere at all. In view of the initial adhesion exploited for protective bonding the lack of adhesion after annealing may seem surprising. However, it may be safely assumed that hydrogen bonds between water molecules adsorbed on the surface oxide layer mediated the initial adhesion. The desorption of the water layer without the reduction of the superficial oxides through atomic hydrogen meant that the wafers could adhere only via van der Waals forces, an interaction much weaker than hydrogen bonding. In the case of this weak interaction, the microroughness of the wafers employed for the present experiments obviously

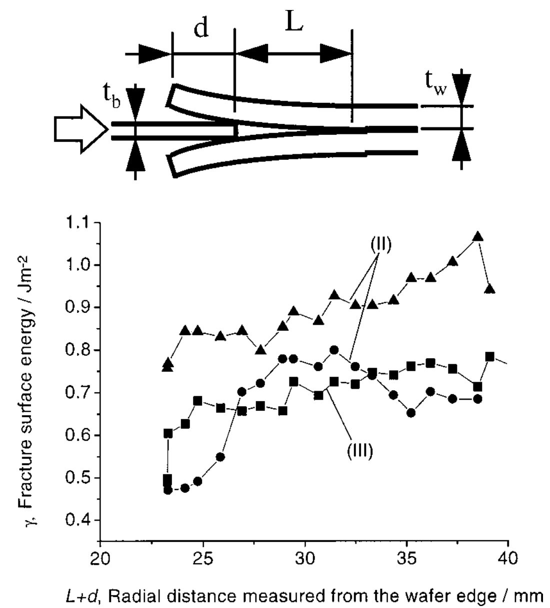

FIG. 2. Fracture surface energy measured by DCB method.

was too large to permit adhesion. Clearly these experiments define a lower limit on the temperature for conventional bonding of oxide-covered GaAs wafers.

B. Interfacial microstructure

First, the interface of the bonding condition (I) is discussed. As mentioned earlier, there was always an unavoidable twist misorientation within ±1.0° between the two wafer crystals (Fig. 3). This twist angle causes a screw dislocation network at the interface. The network was observed for the cases (I) [Fig. 3(a)] and (II) [Fig. 3(b)]. The spacing of the dislocations, 15–30 nm, in fact, corresponds to that which can be calculated from the twist angle between the two crystals, 0.82°, which was measured in the diffraction patterns from a cross-section sample of the same bonded pair

$$d \approx a_{200}/\theta = 0.2825\text{nm}/0.82° = 21.5\text{nm}.$$

This agreement between the spacing of the dislocations and the twist angle acquired from the electron diffractograms could be confirmed for all the other samples. In fact, the network is neither perfectly continuous nor periodical. It may indicate that the interface has not reached the most stable state. Yet, the fact of the network formation suggests that the two wafers have formed a direct interface by covalent bonds.

This agrees with the atomic microstructure observation by high-resolution transmission electron microscopy (HREM) shown in Fig. 4(a). An abrupt interface formed directly without any intermediate layer between the wafers. This indicates that the removal of the oxides was sufficient. Also neither structural disorder nor damage of the lattice was observed. This demonstrates that cleaning with atomic hydrogen not only removes the surface contaminants and surface oxides but also preserves the crystalline structure. In this respect it may be contrasted with other bonding techniques relying on cleaning at high temperatures or ion beam.

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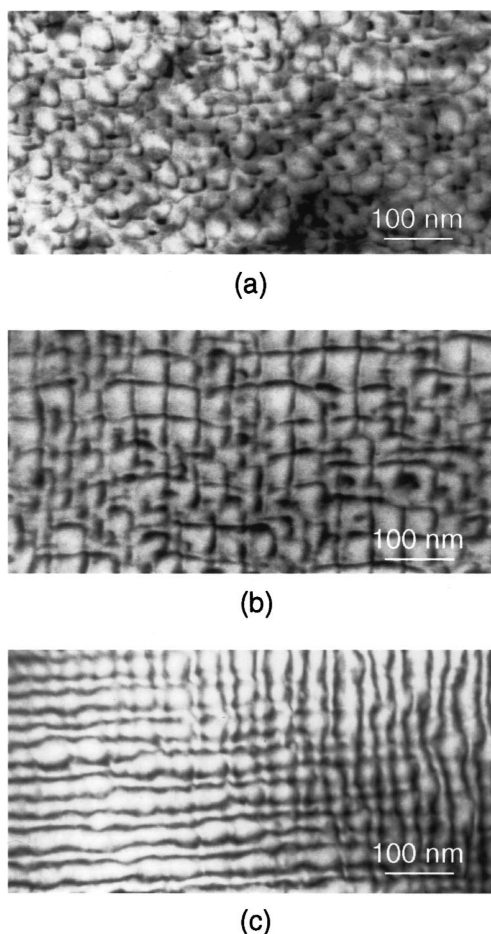

FIG. 3. Plan-view TEMs of the interfaces of conditions: (a) I, (b) II, and (c) III.

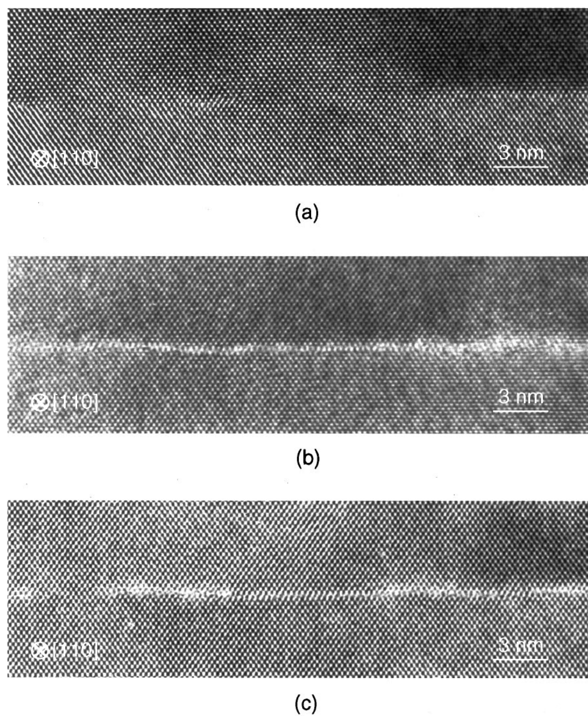

FIG. 4. Cross-sectional HREMs of the interfaces of conditions: (a) I, (b) II, and (c) III.

Edge dislocations can be seen along the interface. These edge dislocations appeared due to the common miscut of the surface plane, tilted off from (001) by nominally $\pm 0.5°$, though the details are yet to be studied.

In the case of the bonding condition (II), the interface formed also a screw dislocation network [Fig. 3(b)]. As mentioned earlier, this indicates that the direct interface formed by covalent bonds. HREM shows also a direct interface [Fig. 4(b)]. However, some regions exhibit a very thin structure of a thickness of a couple of angstroms. Moreover, the interface is partially not flat and has a waviness. First, the origin of such a thin intermediate layer could be attributed to the adsorption of residual gases such as water and oxygen and the surface oxidation by them. The exposure of the wafer surface to the residual gasses until bonding was ~ 6 L ($1\,\mathrm{L} = 10^{-6}\,\mathrm{Torr\,s}$), and that to residual water is estimated to be less than 0.5 L. Accordingly, the possibility of hydroxide formation on the surface before bonding cannot be excluded. Second, the original wafer surfaces do not represent a perfect plane due to the inevitable miscut, waviness, and microscopic roughnesses. These imperfections of the surface plane give rise to surface steps. Under bonding condition (I), the higher bonding temperature may have allowed the atoms to diffuse and form a flat interface. In the case of (II), the bonding temperature of less than 150 °C was probably too low for the atoms to diffuse efficiently and to form a flat interface. Also surface oxides, which might have formed as mentioned earlier, could impede the diffusion.

In the case of (III), the interface also exhibits the very thin structure of a thickness of a couple of angstroms all along the interface [Fig. 4(c)]. A few regions, though only partially, show a clear contrast change at the interface, which indicates another phase, presumably an oxide. The network was hardly confirmed by TEM [Fig. 3(c)]. The lines seen in Fig. 3(c) represent Moiré fringes, the distance of which is half that of the dislocations. As shown in HREM pictures, the Moiré regions occurred at sites where the intermediate layer was found. This layer prevents the network formation along the interface. This difference between (II) and (III) shows that the cleaning condition (III) may not be enough to clean the surface completely.

IV. CONCLUSIONS

We have developed a technique of atomically direct wafer bonding of GaAs by applying atomic hydrogen for cleaning of the surfaces prior to bonding. It has been demonstrated that this method can form an atomically direct and abrupt interface over an area as large as a whole 3 in. wafer. However, no obstacle can be seen in extending it to larger wafer diameters. Moreover, since the process is based on surface cleaning before bonding, no bubbles were detected at the interface, which often occur during the annealing process at high temperatures after conventional wafer direct bonding. In summary, this technique has been shown to have the following positive features:

(1) no wet chemical treatment is necessary,
(2) an abrupt interface without any intermediate layer can be formed,

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(3) no crystallographic damage resulting from the cleaning procedure was found,
(4) the method should be scalable to any wafer diameter, and
(5) since cleaning is carried out as wafers are separate, the subsequent bonding can be carried out at relatively low temperatures. This is important for avoiding thermal strains on bonding materials of dissimilar thermal expansion behavior.

For further understanding of the interface features, it is necessary to investigate the interface formation mechanism, the thermal stability and electronic properties of the interface formed. Control of the joining atmosphere is required for further reduction in bonding temperature. Finally, it can be expected to apply this wafer bonding method to film transfer, and bonding of GaAs to other materials, which are now under investigation by the authors.

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[1] For a recent review, see e.g., A. Plößl and G. Kräuter, Mater. Sci. Eng., R. **25**, 1 (1999).
[2] L. Gordon, G. L. Woods, R. C. Eckardt, R. R. Route, R. S. Feigelson, M. M. Fejer, and R. Byer, Electron. Lett. **29**, 1942 (1993).
[3] Y. S. Wu, R. S. Feigelson, R. K. Route, D. Zheng, L. A. Gordon, M. M. Fejer, and R. L. Byer, J. Electrochem. Soc. **145**, 366 (1998).
[4] G. Patriarche, C. Mériade, G. Le Roux, I. Sagnes, J.-C. Harmand, and F. Glas, *Institute of Physics, 1999*, 11th International Conference on Microscopy of Semiconducting Materials, 22–25 March 1999, Oxford, England.
[5] G. Kästner, T. Akatsu, S. Senz, A. Plößl, and U. Gösele, Appl. Phys. A: Mater. Sci. Precess. (in press).
[6] U. Gösele, H. Stenzel, T. Martini, J. Steinkirchner, D. Conrad, and K. Scheerschmidt, Appl. Phys. Lett. **67**, 3614 (1995).
[7] A. Plößl, S. Mack, H. Stenzel, R. Schol, and U. Gösele, *Proceedings of the International Conference Micro Materials Berlin, Germany, 16–18 April 1997*, edited by B. Michel and T. Winkler (ddp Goldenbogen, Dresden, 1997), pp. 921–924.
[8] H. Takagi, K. Kikuchi, R. Maeda, T. R. Chung, and T. Suga, Appl. Phys. Lett. **68**, 2222 (1996).
[9] T. R. Chung, N. Hosoda, T. Suga, and H. Takagi, Appl. Phys. Lett. **72**, 1565 (1998).
[10] D. L. Miller, R. T. Chen, K. Elliot, and S. P. Kowalszyk, J. Appl. Phys. **57**, 1922 (1985).
[11] D. E. Aspens, W. E. Quinn, and S. Gregory, Appl. Phys. Lett. **56**, 2569 (1990).
[12] T. Van Buuren, M. K. Weilmeier, I. Athwal, K. M. Colbow, J. A. Mackenzie, T. Tiedje, P. C. Wong, and K. A. R. Mitchell, Appl. Phys. Lett. **59**, 464 (1991).
[13] A. Saletes, J. Massies, and J. P. Contour, Jpn. J. Appl. Phys., Part 2 **25**, L48 (1986).
[14] R. W. Bernstein and J. K. Grepstad, J. Vac. Sci. Technol. A **7**, 581 (1989).
[15] A. Takamori, S. Sugata, K. Asakawa, E. Miyauchi, and H. Hashimoto, Jpn. J. Appl. Phys., Part 2 **28**, L7 (1989).
[16] I. Suemune, Y. Kunitsugu, Y. Kan, and M. Yamanashi, Appl. Phys. Lett. **55**, 760 (1989).
[17] I. Suemune, A. Kishimoto, K. Hamaoka, Y. Honda, Y. Kan, and M. Yamanashi, Appl. Phys. Lett. **56**, 2393 (1990).
[18] L. M. Weegels, T. Saitoh, and H. Kanbe, Appl. Phys. Lett. **65**, 3117 (1994).
[19] U. Bischler and E. Bertel, J. Vac. Sci. Technol. A **11**, 458 (1993).
[20] M. Yamada and Y. Ide, Jpn. J. Appl. Phys., Part 2 **33**, L671 (1994).
[21] Y. Ide and M. Yamada, J. Vac. Sci. Technol. A **12**, 1858 (1994).
[22] S. Goto, M. Yamada, and Y. Nomura, Jpn. J. Appl. Phys., Part 2 **34**, L1180 (1995).
[23] E. J. Petit, F. Houzay, and J. M. Moison, J. Vac. Sci. Technol. A **10**, 2172 (1992).
[24] E. J. Petit and F. Houzay, J. Vac. Sci. Technol. B **12**, 547 (1994).
[25] Y. Zhonghai, S. L. Buczkowski, N. C. Giles, and T. H. Myers, Appl. Phys. Lett. **69**, 82 (1996).
[26] C. M. Rouleau and R. M. Park, J. Appl. Phys. **73**, 4610 (1993).
[27] V. Lehmann, U. Gösele, and K. Mitani, Solid State Technol. **33**, 91 (1990).
[28] U. Bischler and E. Bertel, J. Vac. Sci. Technol. A **11**, 458 (1993).
[29] C. Eibl, G. Lackner, and A. Winkler, J. Vac. Sci. Technol. A **16**, 2979 (1998).
[30] K. G. Tschersich and V. von Bonin, J. Appl. Phys. **84**, 4065 (1998).
[31] C. Messmer and J. C. Bilello, J. Appl. Phys. **52**, 4623 (1981).

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