ARTICLE

Sub-nano Layers of Li, Be, and Al on the Si(100) Surface: Electronic Structure and Silicide Formation

Victor Zavodinsky [*] [iD], *Olga Gorkusha* [iD]

Khabarovsk Department of the Institute of Applied Mathematics, Far East Branch of the Russian Academy of Sciences, Khabarovsk, 690022, Russia

ABSTRACT

Within the framework of the density functional theory and the pseudopotential method, the electronic structure calculations of the "metal-Si(100)" systems with Li, Be and Al as metal coverings of one to four monolayers (ML) thickness, were carried out. Calculations showed that band gaps of 1.02 eV, 0.98 eV and 0.5 eV, respectively, appear in the densities of electronic states when the thickness of Li, Be and Al coverings is one ML. These gaps disappear with increasing thickness of the metal layers: first in the Li-Si system (for two ML), then in the Al-Si system (for three ML) and then in the Be-Si system (for four ML). This behavior of the band gap can be explained by the passivation of the substrate surface states and the peculiarities of the electronic structure of the adsorbed metals. In common the results can be interpreted as describing the possibility of the formation of a two-dimensional silicide with semiconducting properties in Li-Si(100), Be-Si(100) and Al-Si(100) systems.

Keywords: Kohn-Sham method; Pseudopotentials; Si(100) surface; Sub-nano metal layers; Density of states; Two-dimensional silicides; Semiconducting properties

1. Introduction

Metal layers on silicon have long attracted the attention of researchers. However, this mainly refers to layers of refractory 3d transition metals that form stable silicides. Layers of low-melting metals on silicon have not been studied enough.

The most indicative include works [1-10], where the atomic and electronic structure of the sub-nano

Li, Be and Al layers on Si(100) and Si(111) surfaces was studied. In the work of Kotllyar et al. [1], the high-temperature interaction of Al with the Si(100) surface at low coverages was studied using low-energy electron diffraction, Auger electron spectroscopy and scanning tunneling microscopy (STM). At low Al coverages (0.05-0.2 ML), the interaction of Al atoms with a top Si(100) substrate layer proceeds by two competitive mechanisms. The first mechanism prevails at Si(100) surface with a low density of missing-dimer defects and resides in the formation of the specific Al-Si clusters. The second mechanism is stimulated by the presence of missing-dimer defects and resides in the substitutional incorporation of Al atoms in the top Si(100) substrate layer. Both mechanisms result in the liberation of the surface Si atoms, which agglomerate into flat islands. In the work of Cocoletzi and Takeuchi [2], the first principles of total energy calculations of the Al induced Si(001)-(3×4) reconstruction are presented; the local density of state images was calculated and compared with the experimental STM measurement. Northrup [3] has studied the adatom-induced reconstruction of the Si(111)√3×√3-Al surface using first-principles pseudopotential total-energy and force calculations. He proposed a new adatom model of this reconstruction wherein each Al adatom sits in a threefold-symmetric site with three first-layer Si neighbors and one second-layer Si neighbor directly below. For this model, the calculated dispersion of the adatom-induced surface states is in good agreement with the experiment. The work of Ko Young-Jo et al. [4] is of particular interest to us, since it describes first-principles calculations of the electronic structure of the Li-Si(100) system, which is one of the objects of our work. They find that Li adatoms interact mainly with the dangling-bond orbitals of Si dimers. The analysis of charge densities demonstrates a large charge transfer from the Li adatom to a dangling-bond orbital of a Si dimer, which is responsible for a large decrease in work function at submonolayer coverages. We will discuss their results in more detail below in comparison with ours. Rysbaev et al. [5] studied the formation of silicide films of metals (Li, Cs, Rb, and

Ba) during ion implantation in Si and subsequent thermal annealing; the effect of ion implantation and subsequent heating on the frequency of surface and bulk plasma oscillations of valence electrons in silicon was described. Hite, Tang and Sprunger [6] used STM and photoelectron spectroscopy to investigate the nucleation, growth, and structure of beryllium on Si(111)-(7×7). They indicated that a chemical reaction occurs at temperatures as low as 120ºK, resulting in a nano-clustered morphology, presumed to be composed of a beryllium silicide compound. Upon annealing to higher temperatures, their data indicate that beryllium diffuses into the selvage region. Saranin et al. [7] studied ordered arrays of Be-encapsulated Si nanotubes on Si(111) surface using STM. Gordeev, Kolotova and Starikov [8] investigated the formation of metastable aluminum silicide as intermediate stage of Al-Si alloy crystallization. They noted that the mechanism of Al-Si alloy crystallization from an amorphous state is still unclear. Despite the absence of equilibrium compounds for this binary system, there are several experimental evidence confirming the formation of metastable silicide at annealing of amorphous Si mixed with Al. The authors considered the properties of the aluminum Al_2Si silicide structure, which is a probable candidate for the role of the observed metastable compound. Their investigation was based on the atomistic simulations with the interatomic potential and density functional theory approach. All used methods revealed that there are several crystal structures of Al_2Si with close geometry and relatively low formation energies. The chemical ordering in such structures is similar to the one in Si-Al melt. The authors also showed that the combination of these structures allows to form a crystal with different degrees of ordering. Terekhov et al. [9] have studied the possibility of the metastable Al_3Si phase formation in composite Al-Si films obtained by ion-beam and magnetron sputtering. Endo et al. [10] made an elementary analysis of each atom on the Si surface, and metal atoms on the Si(001) surface by STM and spectroscopy; the result was evaluated with the first principles calculations. As metallic contaminations, sub-monolayer of alu-

minum was evaporated on the Si(001)-2×1 surface. The local density of states on the Al/Si(001)-2×1 was measured by scanning tunneling spectroscopy at room temperature. Experimental results are in good agreement with those obtained from the calculations.

Unfortunately, we were unable to find publications (experimental or theoretical) concerning the electronic structure of the Be-Si(100) and Al-Si(100) systems. As for the Li-Si system, the work presents the results of calculations only for lithium layers of 0.5 and 1.0 ML and band gap of 1.35 eV width was found for one ML. However, almost all of the works listed above indicate the possibility of forming two-dimensional silicides when sub-nano layers of lithium, berlium and aluminum are deposited on the silicon surface. At the same time, there are publications indicating that two-dimensional silicides may have semiconductor properties. For example, in the work of Clark et al. [11] it was shown, as a result of calculations from first principles, that a nanolayer of the iron dislicide with a band gap of 0.73 eV can grow epitaxially on the Si(100) surface. The results indicate that the appearance of semiconductor properties is also possible when such a light metal as lithium is deposited on silicon, and it is necessary to check this possibility for other light metals, in particular for beryllium and aluminum. In order to clarify the possibility of silicide formation with semiconductor properties in Li-Si(100), Be-Si(100) and Al-Si(100) nanosystems, we fulfilled the study of these systems by computer simulation using the Kohn-Sham method [12] within the framework of the density functional theory [13] and the pseudopotential method [14]. Since this approach involves performing calculations only at 0°K, we considered these systems with disordered metal layers.

2. Research methodology

All calculations were performed using the FHI96md package [15]. Pseudopotentials were found using the FHI98pp package [14]. To calculate the exchange-correlation energy, the local electron density approximation was used [16,17]. In all cases, the cutoff energy of a set of plane waves was taken to be 14 Ry;

calculations were carried out with the five k-points: (0.5; 0.5; 0.5), according to the $3 \times 3 \times 1$ scheme, in a supercell with dimensions $14.54 \times 14.54 \times 40$ (all values are given in atomic units, one atomic unit is equal to 0.529 Å). The electronic structure was studied by calculating the density of electronic states (DOS), for which each electronic level was smeared using a Gaussian function with a half-width of 0.05 eV or 0.025 eV. The last half-width was used in cases with a narrow band gap. We took a Si slab consisting of four monolayers (ML) as a silicon substrate with a Si(100) surface. Each ML contained four atoms, and the lowest ML was terminated with eight hydrogen atoms. Thus, due to the periodic boundary conditions in the X and Y directions, we studied a thin infinite plate, and the large value of the parameter c (40 atomic units) for the supercell ensures that there is no interaction between the virtual plates in Z dimension.

The atoms of the lowest ML of silicon were fixed; the atoms of the remaining layers, as well as the ML atoms of the studied metals, could move under the action of quantum mechanical interatomic forces.

Each metal ML also contained four atoms. Their deposition was carried out in a disordered manner using a special program developed by us based on a random number generator. To make sure that the band gap arises precisely during the interaction of silicon with metal, we also calculated the DOS for metal layers taken separately from the silicon substrate.

3. Results and discussion

Our calculations showed that for the metals studied, the arrangement of their atoms on the Si(100) surface turned out to be rather different. Schemes of the optimized arrangement of atoms for one ML metal-Si(100) system are presented in **Figure 1**.

It can be seen that, under the influence of the structure of the silicon surface, some ordering of the arrangement of metal atoms occurred, but in all cases, the structure of the metal monolayers is still far from epitaxial. The structure of systems with a greater number of monolayers than one ML became

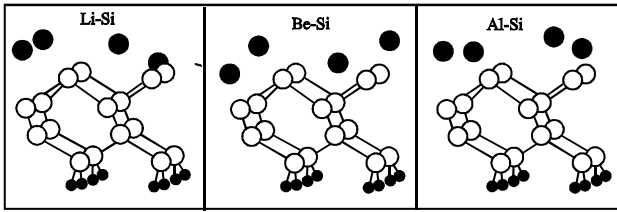increasingly disordered with increasing thickness.

Figure 1. Arrangement of atoms in the Li-Si, Be-Si and Al-Si systems when the first disordered metal monolayers are deposited on the Si(100) surface. White circles are silicon atoms, big black circles are metal atoms, small black circles are hydrogen atoms.

Figure 2 shows the distribution patterns of the density of states formed when the first monolayers of Li, Be and Al are deposited on the surface. The DOS for a clean Si(100)-2×1 surface with the gap of 0.35 eV is also shown there. Note that the reconstruction of the surface structure Si(100)→Si(100)-2×1 occurred spontaneously during the relaxation of the free Si(100) surface, and during calculations with adsorbed metal layers, the reconstruction disappeared.
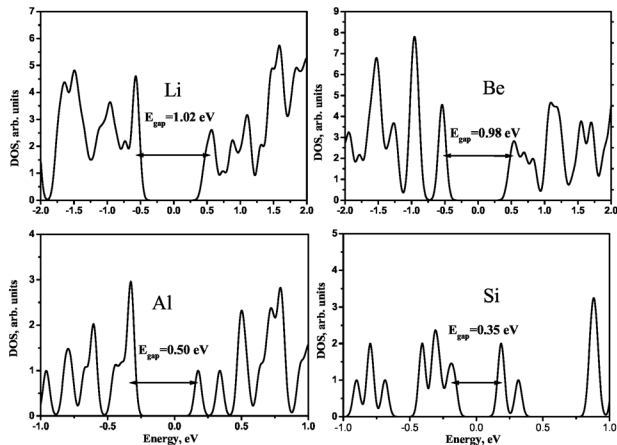

Figure 2. Density of electronic states formed when the first monolayer of Li, Be and Al is deposited on the Si(100) surface in comparison with the density of states for a clean Si(100)-2×1 surface. The Fermi level corresponds to zero energy.

From this figure, it is clear that in all cases there is an energy gap near the Fermi level: 1.02 eV for Li-Si, 0.98 eV for Be-Si and 0.50 eV for Al-Si. The band gap we obtained for the Li-Si system is significantly less than the 1.35 eV value [4]. This can be explained by the fact that Ko et al. provide data for an ordered Li monolayer on Si(100), while we ex-

amined the Li-Si(00) system with a disordered monolayer of Li. For the clean Si(100)-2×1 surface, we obtained 0.35 eV in good agreement with the known data given in published works: 0.4 eV (electron energy loss spectroscopy) [18], 0.5 eV (scanning tunneling spectroscopy) [19], and 0.2-0.3 eV (calculations from first principles) [20]. At the same time, we did not detect an energy gap in the electronic structure of Li, Be and Al metal monolayers without a silicon substrate (**Figure 3**). Unfortunately, we do not have data on the electronic structure of Be-Si(100) and Al-Si(100) systems, so we cannot compare our results with published ones. However, since our results for pure silicon and for lithium on silicon are close to those published, we have reason to believe that the results we obtained for the Be and Al on Si(100) are also quite reliable.
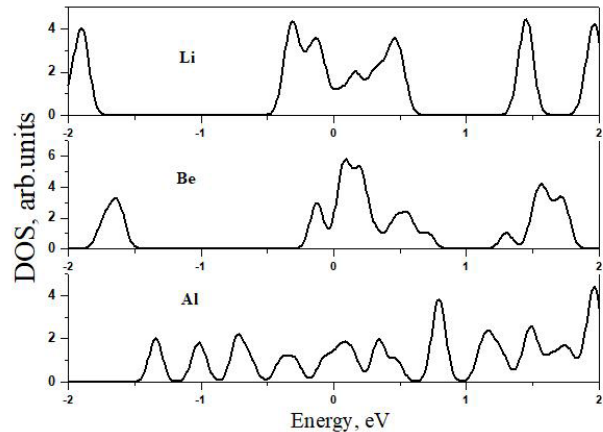

Figure 3. DOS corresponding to monolayers of Li, Be and Al taken separately from the silicon substrate.

The deposition of the second ML led to the fact that in the Li-Si system, the gap in the density of states disappeared. In the Be-Si system, it decreased to 0.61 eV, and in the Al-Si system, it increased to 0.62 eV, which is illustrated in Figure 4 (top panels). In contrast, the DOS for two ML of Li, Be and Al without a substrate has a metallic character, as can be seen in the same figure (bottom panels), as in the case of a single ML.

We did not examine the Li-Si system during the deposition of the third ML, since we were interested in the presence of an energy gap, and in this system the gap disappeared already with two metal ML.

The DOS for the Be-Si and Al-Si systems are shown in **Figure 5** (top panels). In the Be-Si system, the gap decreased to 0.27 eV, and in the Al-Si system, it completely disappeared. Calculation of three monolayers of beryllium and aluminum separately from silicon demonstrated the metallic nature of their DOS (see **Figure 5**, bottom panels).
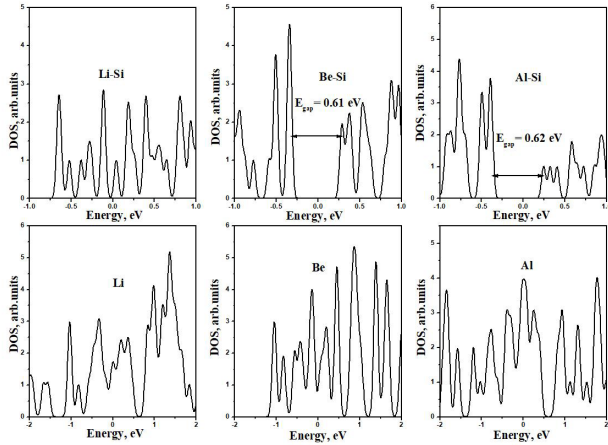

Figure 4. Densities of states of Li-Si, Be-Si and Al-Si systems for two metal monolayers. On the bottom panels there is a DOS for two monolayers of Li, Be and Al, taken separately from the silicon substrate.
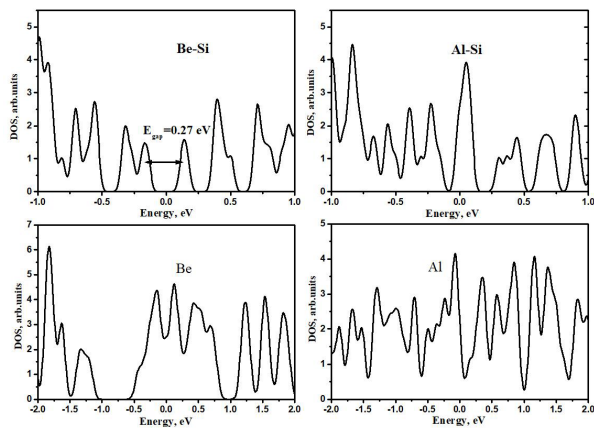

Figure 5. DOS for Be-Si and Al-Si systems with three metal monolayers. Here (on the bottom panels) is a DOS for three monolayers of Be and Al, taken separately from the substrate.

To find out whether the energy gap in the Be-Si system will disappear when another (fourth) Be monolayer is deposited on the silicon surface, we carried out the corresponding calculations and plotted the density of states in **Figure 6**.

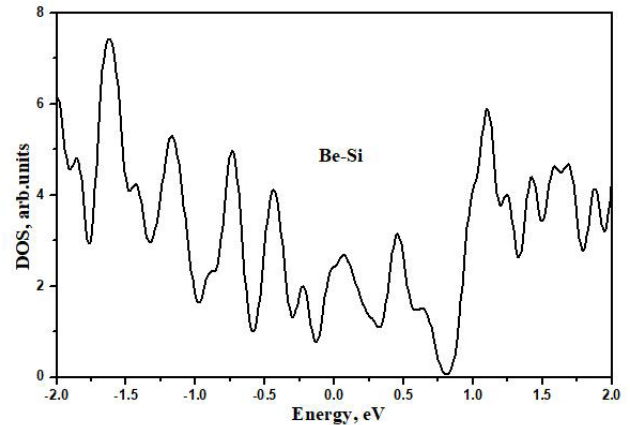From this figure, it is clear that the DOS for the Be-Si system with four ML of beryllium has a metal-lic character.

Figure 6. DOS for the Be-Si system with four metal monolayers.

Thus, the obtained results show that in disordered Li-Si(100), Be-Si(100) and Al-Si(100) systems with sub-nano metal layers, electronic structures with band gaps are formed, and the bands disappear with increasing thickness of the deposited metal layers.

4. Conclusions

Electronic structure calculations by the Kohn-Sham method using pseudopotentials showed that in the densities of electronic states of two-dimensional "metal-Si(100)" systems with Li, Be and Al disordered layers of the one ML thickness, band gaps with widths of 1.02 eV, 0.98 eV and 0.5 eV, respectively, appear. These gaps disappear with increasing thickness of the metal layers: first in the Li-Si system (for two ML), then in the Al-Si system (for three ML) and then in the Be-Si system (for four ML).

It seems to us that our results can be interpreted as the discovery of the possibility of forming two-dimensional silicides of lithium, beryllium and aluminum with semiconducting properties. This assumption correlates with the conclusions expressed in the works we cited in the Introduction.

Typically, the formation of silicides is accompanied by mixing of metal and silicon atoms. In our case, mixing does not occur, which is apparently explained by the zero temperature of the calculation. However, there is another important characteristic of silicides that should manifest itself in two-di-

mensional silicides, namely the formation of strong chemical bonds between the metal layers and the silicon surface atoms. The energy value characterizing the magnitude of these forces is the adhesion energy. We calculated the adhesion energy (E_{adh}) and obtained the following values: $E_{adh}(Li) = 1.67$ J/m^2, $E_{adh}(Be) = 1.68$ J/m^2, $E_{adh}(Al) = 2.05$ J/m^2. For comparison, we carried out test calculations for 1 ML Fe on the surface of Si(100), and obtained an adhesion energy of 4.5 J/m^2, which is 2-2.5 times higher than our values. Perhaps this is because iron has 8 valence electrons versus 1, 2 and 3 in Li, Be and Al. Besides, when the thickness of the metal layer becomes greater, its non-order increases, which also affects the decrease in the band gap. Therefore, in our case, the values of adhesion energy are sufficient to form two-dimensional silicides. In our opinion, such systems can be used to create two-dimensional semiconductor devices.

Authors' Contributions

Victor Zavodinsky: concept, review, discussion of results, writing the article.

Olga Gorkusha: performing calculations, constructing figures, discussing the results.

Conflict of Interest

The authors have no conflict of interest with anyone.

References

[1] Kotlyar, V.G., Saranin, A.A., Zotov, A.V., et al., 2002. High-temperature interaction of Al with Si(100) surface at low Al coverages. Surface Science. 506(1-2), 80-86.
DOI: https://doi.org/10.1016/S0039-6028(01)01768-X

[2] Cocoletzi, G.H., Takeuchi, N., 2002. First principles total energy calculations of the Al induced Si (0 0 1)-(3×4) reconstruction. Surface Science. 504, 101-107.
DOI: https://doi.org/10.1016/S0039-6028(01)01915-X

[3] Northrup, J.E., 1984. Si(111)√3×√3-Al: An adatom-induced reconstruction. Physical Review Letters. 53(7), 683-686.
DOI: https://doi.org/10.1103/PhysRevLett.53.683

[4] Ko, Y.J., Chang, K.J., Yi, J.Y., 1997. Atomic and electronic structure of Li-adsorbed Si(100) surfaces. Physical Review B. 56(15), 9575.
DOI: https://doi.org/10.1103/PhysRevB.56.9575

[5] Rysbaev, A.S., Normurodov, M.T., Khujaniyozov, J.B., et al., 2021. On the formation of silicide films of metals (Li, Cs, Rb, and Ba) during ion implantation in Si and subsequent thermal annealing. Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques. 15(3), 607-610.
DOI: https://doi.org/10.1134/S10274510210303

[6] Hite, D.A., Tang, S.J., Sprunger, P.T., 2003. Reactive epitaxy of beryllium on Si (1 1 1)-(7×7). Chemical Physics Letters. 367(1-2), 129-135.
DOI: https://doi.org/10.1016/S0009-2614(02)01637-8

[7] Saranin, A.A., Zotov, A.V., Kotlyar, V.G., et al., 2004. Ordered arrays of Be-encapsulated Si nanotubes on Si (111) surface. Nano Letters. 4(8), 1469-1473.

[8] Gordeev, I., Kolotova, L., Starikov, S., 2022. Formation of metastable aluminum silicide as intermediate stage of Al-Si alloy crystallization. Scripta Materialia. 210, 114481.
DOI: https://doi.org/10.1016/j.scriptamat.2021.114481

[9] Terekhov, V.A., Usoltseva, D.S., Serbin, O.V., et al., 2018. Possibility of the metastable Al$_3$Si phase formation in composite Al-Si films obtained by ion-beam and magnetron sputtering. Condensed Matter and Interphases. 20(1), 135-147.
DOI: https://doi.org/10.17308/kcmf.2018.20/485

[10] Endo, K., Arima, K., Kataoka, T., et al., 1998. STM/STS and the first principles calculations on Al/Si (001) 2×1. Applied Physics A. 66, S145-S148.
DOI: https://doi.org/10.1007/s003390051118

[11] Clark, S.J., Al-Allak, H.M., Brand, S., et al., 1998. Structure and electronic properties of FeSi$_2$. Physical Review B. 58(16), 10389.
DOI: https://doi.org/10.1103/PhysRevB.58.10389

[12] Kohn, W., Sham, L.J., 1965. Self-consistent equations including exchange and correlation effects. Physical Review. 140(4A), A1133.

DOI: https://doi.org/10.1103/PhysRev.140.A1133

[13] Hohenberg, P., Kohn, W., 1964. Inhomogeneous electron gas. Physical Review. 136(3B), B864.

DOI: https://doi.org/10.1103/PhysRev.136.B864

[14] Fuchs, M., Scheffler, M., 1999. Ab initio pseudopotentials for electronic structure calculations of poly-atomic systems using density-functional theory. Computer Physics Communications. 119(1), 67-98.

DOI: http://dx.doi.org/10.1016/S0010-4655(98)00201-X

[15] Bockstedte, M., Kley, A., Neugebauer, J., et al., 1997. Density-functional theory calculations for poly-atomic systems: Electronic structure, static and elastic properties and ab initio molecular dynamics. Computer Physics Communications. 107(1-3), 187-222.

DOI: http://dx.doi.org/10.1016/S0010-4655(97)00117-3

[16] Ceperley, D.M., Alder, B.J., 1980. Ground state of the electron gas by a stochastic method. Physical Review Letters. 45(7), 566.

DOI: https://doi.org/10.1103/PhysRevLett.45.566

[17] Perdew, J.P., Zunger, A., 1981. Self-interaction correction to density-functional approximations for many-electron systems. Physical Review B. 23(10), 5048.

DOI: https://doi.org/10.1103/PhysRevB.23.5048

[18] Gavioli, L., Betti, M.G., Cricenti, A., et al., 1995. Surface electronic structure at Si (100)-(2x1). Journal of Electron Spectroscopy and Related Phenomena. 76, 541-545.

[19] Hata, K., Shibata, Y., Shigekawa, H., 2001. Fine electronic structure of the buckled dimers of Si(100) elucidated by atomically resolved scanning tunneling spectroscopy and bias-dependent imaging. Physical Review B. 64(23), 235310.

DOI: https://doi.org/10.1103/PhysRevB.64.235310

[20] Fritsch, J., Pavone, P., 1995. Ab initio calculation of the structure, electronic states, and the phonon dispersion of the Si(100) surface. Surface Science. 344(1-2), 159-173.

DOI: https://doi.org/10.1016/0039-6028(95)00802-0