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Structures and electrical conductance at the initial stages of magnesium growth on Si(111)-Pb surface

M. V. Ryzhkova [1] ✉, D. A. Tsukanov [1]

[1] Institute of Automation and Control Processes Far Eastern Branch of the RAS, Vladivostok, Russia

✉ lavric@iacp.dvo.ru

Abstract: In the present work, we have studied the growth of Mg ultrathin films on the Si(111) surface modified by Pb reconstructions using low-energy electron diffraction and the four-point-probe method. The new binary surface reconstructions √7×√7-(Mg, Pb) and √19×√3-(Mg, Pb) have been observed for the first time. The growth of magnesium layers depends both on the structure of Pb-induced surface reconstruction and on the Mg deposition manner. It is assumed that inclusion of magnesium atoms in the √7×√7 surface structure stabilizes the growth of Mg film which is independent of the manner of deposition in this case. We have investigated surface electrical conductance after the formation of magnesium layers at room temperature until about 9 monolayers of Mg coverage. In addition to the magnesium film Mg(0001), the highest electrical conductance among the presented surface structures has been detected for the Si(111)-6×6-(Pb, Mg) surface phase that consists of the maximum number of metal atoms, both lead and magnesium.

Keywords: silicon, electrical conductance, surface structures, metal films, low-energy electron diffraction

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Материалы конференции
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Структуры и электрическая проводимость на начальных стадиях роста Mg на Si(111)-Pb

М. В. Рыжкова [1] ✉, Д. А. Цуканов [1]

[1] Институт автоматики и процессов управления Дальневосточного отделения РАН, г. Владивосток, Россия

✉ lavric@iacp.dvo.ru

Аннотация. В данной работе с помощью дифракции медленных электронов и четырехзондового метода измерения электрической проводимости изучен рост сверхтонких пленок Mg на поверхности Si(111), модифицированной поверхностными фазами свинца. Поверхностные структуры √7×√7-(Mg, Pb) и √19×√3-(Mg, Pb) были получены впервые. Рост слоев магния зависит как от структуры поверхности, модифицированной Pb, так и от способа осаждения Mg. Предполагается, что включение атомов магния в структуру поверхности √7×√7 стабилизирует рост пленки Mg, который в данном случае не зависит от способа осаждения. Мы исследовали электрическую проводимость поверхности после формирования слоев магния при комнатной температуре до покрытия примерно 9 монослоями магния. Помимо пленки магния Mg(0001), наибольшая электрическая проводимость среди представленных поверхностных структур обнаружена для поверхностной фазы Si(111)-6×6-(Pb, Mg), состоящей из максимального числа атомов металла.

Ключевые слова: Кремний, электрическая проводимость, поверхностные структуры, металлические пленки, дифракция медленных электронов

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Introduction

Adsorption of metals on the silicon surface leads to the formation of ultrathin films or other nanostructures and attracts attention from the fundamental point of view as well as of practical interest. In particular, adsorption of magnesium has been intensively studied for the past few years because of the possible application in optoelectronics of the Mg_2Si silicide which is a narrow band gap semiconductor. The growth of Mg-induced superstructures and thin films has been examined previously by several groups [1–5]. It is known that adsorbed magnesium atoms on Si(111)-7×7 surface form a silicide layer at room temperature [1]; specifically, it features the first layer as a silicide formation [1–3], dependence of the growth mode on the flux rate [1, 3] or dependence on the deposition manner [4]. Given high flux rates (at relatively large doses) of magnesium deposition, in the first instance, a Mg_2Si silicide film is formed with the structure of $2/3\sqrt{3}\times2/3\sqrt{3}$ [1–4], followed by the growth of a polycrystalline magnesium film [1–4]. At low flux rate or small Mg doses, silicide islands grow starting from the initial stage of deposition, followed by the growth of a polycrystalline magnesium film [4].

In all cases, a large mass transport of silicon takes place and the resulting surface morphology must be quite complicated. However, when magnesium is deposited onto the 1×1-Pb reconstructed surface, some ordered superstructures, 4×4-(Mg, Pb) or 6×6-(Mg, Pb) [6, 7], are formed, and silicon mass transport is hindered up to 1 monolayer (ML) of adsorbed magnesium coverage. Such conditions have a strong impact on the growth of epitaxial film with an abrupt interface for a reactive system such as the Mg/Si(111) one.

In this work, we have studied the influence of surface reconstructions formed by preliminary Pb deposition on the growth of magnesium films. Moreover, Mg was deposited at room temperature on various surfaces containing both Pb and Mg atoms. The structural ordering of Si(111)-(Mg,Pb) systems was studied by low-energy electron diffraction (LEED) and surface conductance was investigated by four-point-probe (4PP) measurements *in situ*.

Materials and Methods

The experiments were performed in the dual ultrahigh vacuum chamber with a base pressure of 2×10^{-10} Torr. Silicon specimens with (111) surface orientation were used. All samples were *n*-type (P-doped) with the nominal electrical resistivity of 20 – 100 Ohm·cm. The sizes of specimen were $15\times5\times0.3$ mm^3. Mg was deposited from a heated tantalum cell at rate of 0.6 ML/min. A magnesium amount was calibrated by the formation of 4×4-(Pb, Mg) and 6×6-(Pb, Mg) (Fig. 1, *a*, *d*) surface reconstructions, which were formed at 0.4 ML and 1 ML of magnesium coverage, respectively [6, 7]. These phases were created at room temperature so there was no desorption of Mg atoms from the surface. Pb was deposited from heated Ta tube at rate of 0.4 ML/min. Pb was calibrated by formation of 1×1-Pb surface structure containing 1 ML of Pb. Surface structures of the (Pb, Mg)/Si(111) systems were observed by LEED. Surface conductance of the samples was measured by the *in situ* 4PP method where probes are arranged in square cones with the interprobe distance of 0.6 mm. The measured resistance values ($R_{measure}$) were converted into a surface conductance σ according to the formula

$$\sigma(S/\square) = \frac{\ln(2)}{2\pi R_{measure}}.$$

According to this formula, the surface conductance of the bared Si(111)-7×7 sample before the deposition experiments was $7.6 \pm 0.5 \cdot 10^{-5}$ S/□.

Results and Discussion

Figure 1, *a* – *e* shows the LEED patterns observed after Mg adsorption onto the Si(111)-1×1-Pb reconstructed surface at room temperature. It is evident that Mg deposition up to 1 ML coverage leads to a series of consistent transformations of the surface structures. The 4×4 periodicity in (Fig. 1, *a*) was obtained after the adsorption of 0.4 ML of magnesium. After Mg deposition of 0.5 ML, the LEED pattern of so-called 'perforated ribbons' phase [6] is observed (Fig. 1, *b*) while the LEED pattern 6√3×6√3 at more than 0.5 ML is seen quite well in the LEED picture together with 4×4 spots (Fig. 1, *c*). With a further increase of the magnesium coverage, a 6×6 (1 ML of Mg) structure is formed (Fig. 1, *d*). At coverage slightly above 1 ML and up to 7 ML the corresponding LEED patterns show a 2×2 periodicity (Fig. 1, *e*). It should be noted that the LEED patterns at this stage of deposition are different depending on the manner of deposition.

At Mg coverage up to 1 ML, it makes no difference whether magnesium is deposited in large or small portions. However, in the case when magnesium is deposited in large doses (each dose is about 2 ML at a time), a 4×4 periodicity appears in the LEED pattern above 2 ML (Fig. 1, *f*) instead of the 2×2 one. After deposition of small Mg doses (each dose is about 0.2 – 0.5 ML at a time), the LEED pattern has shown the 2×2 periodicity. A mixture of 2×2 and 4×4 structures were often observed at average portions of adsorbed Mg. It is suggested in [4] that magnesium grown depends strongly on the deposition manner. It was shown that deposition of large Mg portions of about 4 – 10 ML led to the formation of a silicide film followed by the growth of magnesium islands, while deposition of small Mg portions of about 0.1 ML [4] results in the formation of silicide islands. According to [6], magnesium atoms penetrate under the Pb layer and form stable ties with Si and Pb atoms. During deposition, Pb atoms float on top of the magnesium layer. Therefore, we can assume that Pb atoms form both the 4×4 periodicity and the 2×2 one on the surface of two types of islands formed at large and small portions of deposition, respectively.

Figure 2 illustrates the effect of Mg deposition on the surface conductance of Si(111) samples covered by Pb-induced or binary (Pb, Mg)-induced surface reconstructions. In the case of Mg deposition onto the Si(111)-1×1-Pb surface, some decrease in the surface conductance was

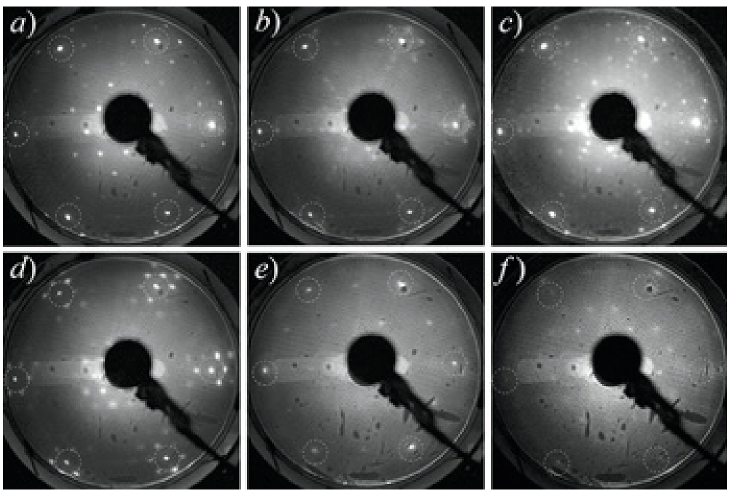

Fig. 1. LEED patterns (40eV) of surface structures formed on Si(111)-1×1-Pb surface at room temperature after Mg deposition. Dashed circles indicate the 1×1 spots;
4×4-(Pb, Mg) with 0.4 ML of Mg (*a*); 'perforated ribbons' with 0.5 ML of Mg (*b*); 6√3+4×4-(Pb, Mg) structure with 0.5 ML of Mg (*c*); 6×6-(Pb, Mg) with 1 ML of Mg (*d*); 2×2-(Pb, Mg) with 7 ML of Mg at small doses (*e*); 4×4-(Pb, Mg) with 9 ML of Mg at large doses (*f*).

established (Fig. 2). Formation of the 6√3×6√3 structure at 0.5 ML of Mg results in the minimum conductance that is extended up to 1 ML magnesium coverage. With a further increase of magnesium coverage (6×6 structure), surface electrical conductance begin to increase. According to [7], the work function increases in the range of 0 – 0.5 ML, which is a fairly natural picture inherent in the deposition of alkali and alkaline earth metals [8, 9], and the resulting band bending leads to a decrease in conductance (see Fig. 2). However, when the 6×6 structure appears, surface electrical conductance increases due the formation of a continuous metal layer. Recently, the presence of metallic states in the Si(111)-6×6-(Mg, Pb) surface phase was confirmed by data of angle-resolved photoemission spectroscopy (ARPES) [6].

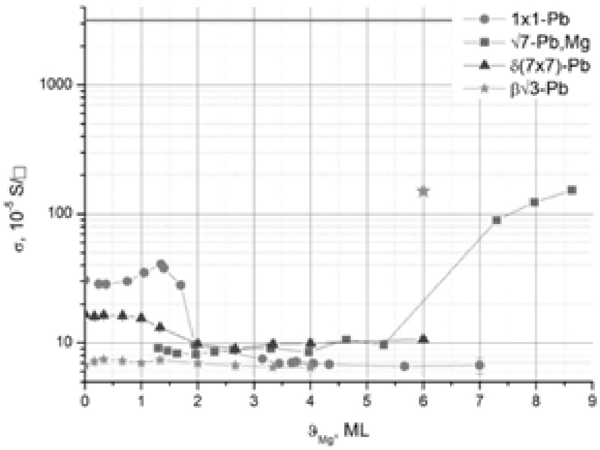

Fig. 2. Surface electrical conductance of surface structures at magnesium deposition.

After the further deposition of magnesium atoms, conductance begins to decrease until 7 ML of Mg depending on the manner of deposition. At large portions of adsorbed Mg (about 2 ML at a time), the corresponding surface electrical conductance was $13.7 \cdot 10^{-5}$ S/□ whereas at small portions (0.2 – 0.5 ML at a time) surface electrical conductance appeared to be $7 \cdot 10^{-5}$ S/□.

At the next stage, magnesium was deposited at room temperature onto the Si(111)-β√3×√3-Pb reconstructed surface contained the 0.33 ML of Pb [10, 11]. It was observed that √3×√3 superspots in the LEED pattern are fainted gradually while the 1×1 periodicity disappeared only at 6 ML of adsorbed Mg coverage leaving the high background on the screen. Deposition of large portions of Mg leads to appearance of LEED '1×1' spots that are specific to the grown magnesium film with the Mg(0001) orientation (Fig. 3, *a*). This magnesium film demonstrated a relatively high conductivity value (marked by stars in Fig. 2) of $150 \cdot 10^{-5}$ S/□, which is however lower then the calculated value $3189 \cdot 10^{-5}$ S/□ for the Mg layer of 1.4 nm (Fig. 2, horizontal line). It was established for the LEED picture that this metal film has a polycrystalline structure (Fig. 3, *a*) because the spots look like arcs meaning a large number of defects on the surface. The ratio of lattice constants was evaluated as Si/Mg = 3.84Å/3.21Å = 1.196, that is, 1/1.196 = 0.84 in reciprocal space. The LEED pattern was used to measure the Si/Mg ratio as 0.86, which is very close to the calculated value (Fig. 3, *a*).

A structure known as a δ(7×7) was observed upon Mg deposition onto the Pb layer preliminarily formed by lead adsorption at room temperature onto the Si(111)-7×7 bared surface. The LEED pattern has shown a gradual uniform decay of diffraction spots following with background after 2.5 ML of deposited Mg. Figure 2 shows the changes in surface conductance (triangles), exhibiting a smooth decrease in conductance after 1 ML of adsorbed Mg reaching the constant value of $1 \cdot 10^{-4}$ S/□ coverage at about 2 ML of Mg. In that case, electrical conductance is significantly higher than that for the Mg deposited on the β√3-Pb surface due to the lower

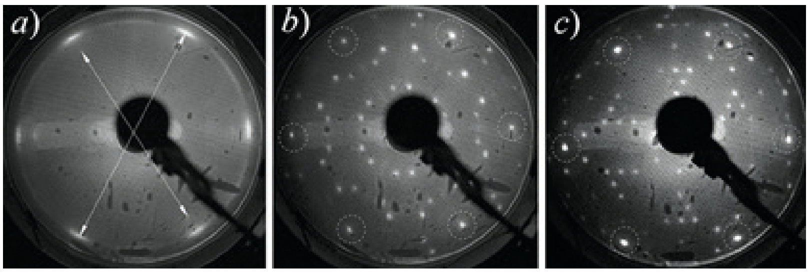

Fig. 3. LEED patterns (40 eV) for magnesium film Mg (0001) of 1.4 nm (*a*); √7×√7-(Pb,Mg) (*b*); √3×√19-(Pb,Mg) (*c*), dashed circles indicate the 1×1 spots.

initial surface electrical conductance of the β√3-Pb sample as compared to the δ(7×7) one (Tab. 1).

Figure 2 shows the changes in the surface electrical conductance during magnesium deposition on the surface phase Si(111)-√7×√7-(Pb, Mg) which already contains both Pb and Mg atoms (squares). The optimal conditions for preparation of this structure are the following: 1 – 1.3 ML of magnesium deposited onto the Si(111)-β√3×√3-Pb surface phase, followed by heating the sample for 30 seconds at 250 °C. The LEED pattern has shown a gradual decay of √7×√7 (Fig. 3, *b*) superspots up to 2.6 ML of adsorbed Mg, then fading of the 1×1 spots intensity is observed and finally the ring appears in the LEED pattern indicating the formation of magnesium film at Mg coverage of 7 ML. This ring is identical to the case of Mg deposition onto the Si(111)-β√3×√3-Pb surface (large Mg portions) (Fig. 3, *c*). It was concluded that formation of the magnesium layer does not depend on the manner of deposition in this case due to a stabilizing role of magnesium in the √7×√7 surface phase. The surface electrical conductance slightly changed until the Mg coverage reached the 5.5 ML and further the conductance began to increase due to the formation of magnesium film.

As indicated in Table 1, an increase in metal coverage in the studied structures results in increase in conductance except for some cases. For example, in the case of √7×√7-(Pb, Mg) structure the conductance value is higher than that for the β√3×√3-Pb one but if the same amount of magnesium is deposited onto the β√3×√3-Pb surface at room temperature conductance is not changed (Fig. 2) due to islanding of adsorbed species. In the case of another structure contained magnesium, Si(111)-√19×√3-(Pb, Mg) (Fig. 3, *c*), obtained by deposition of 0.6 – 0.9 ML of Mg onto the β√3×√3-Pb surface followed by heating the sample for 30 seconds at 350 °C, the electrical conductance is slightly lower than that for the √7×√7-(Pb, Mg) surface phase because the total amount of metal atoms, Mg and Pb, is smaller. The highest electrical conductance among the presented surface structures, except for the magnesium film Mg(0001), was demonstrated for the Si(111)-6×6-(Pb, Mg) surface phase which has a maximum amount of metal atoms, both Pb and Mg, in the structure, 2 ML in total.

Table 1

Surface electrical conductance σ and metal compounds for some surface structures

Structures	σ, 10^{-5} S/□	Θ_{sum}, ML	Θ_{Pb}, ML	Θ_{Mg}, ML
β√3√×3Pb	6.7	0,3	0,3	0
δ(7×7)-Pb	16.6	1	1	0
1×1-Pb	30.7	1	1	0
√3×√19-(Pb, Mg)	6.7	0.9	0.3	0.6
4×4-(Pb, Mg)	28.5	1.4	1	0.4
√7×√7-(Pb, Mg)	9.1	1.3	0.3	1
6×6-(Pb, Mg)	40.8	2	1	1
6√3×6√3-(Pb, Mg)	28.4	1.7	1	0.7
Mg(0001) of 8.6 ML	152.7	8.9	0.3	8.6

Conclusion

Growth of Mg films depends on the deposition manner of magnesium atoms in all cases except for the formation Mg film on the √7×√7-(Pb, Mg). Deposition of the large portions of Mg atoms (about 1-2 ML at once) results in the formation of Mg (0001) polycrystalline film. The small portions (about 0.5 – 1 ML at once) lead to disordered film formation. The corresponding electrical conductance is higher for the magnesium film and lower for the disordered layers. Magnesium growth on the √7-(Pb, Mg) surface does not depend on the deposition manner. New surface phases containing the Mg and Pb atoms have been obtained, √7×√7-(Pb, Mg) and √19×√3-(Pb,Mg) ones.

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THE AUTHORS

RYZHKOVA Maria V.
lavric@iacp.dvo.ru
ORCID: 0000-0001-8990-7140

TSUKANOV Dmitry A.
tsukanov@iacp.dvo.ru
ORCID: 0000-0002-8900-3480

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