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Thermal evolution of the morphology of Ni/Ge(111)-c(2 × 8) surface

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The thermal evolution of the interface formed by room temperature (RT) deposition of Ni atoms (coverage 0.1, 0.5, 1.2 ML) onto a Ge(111)-c(2 × 8) surface has been studied with the use of scanning tunneling microscopy (STM). Atomically resolved STM images revealed that, at RT, the boundaries between the different c(2 × 8) domains acted as nucleation sites for Ni atoms. After annealing the surface with deposited material at 473 to 673 K the formation of nano-sized islands of Ni_xGe_y compounds was observed. In addition, the occurrence of ring-like structures was recorded. Based on the dual-polarity images the latter were assigned to Ni atoms adsorbed on Ge adatoms.

Keywords: Ge(111); Ni; nickel germanides; scanning tunneling microscopy

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1. Introduction

Although the first transistor was made of germanium, there is no doubt that the modern semiconductor industry has been dominated by silicon [1]. Both materials take the diamond crystal structure in solid phase and have an indirect energy gap with similar electronic structure. However, in contrast to silicon, germanium has a lower melting point and its oxide is water soluble, which makes this material less useful from the technological point of view. Differences between these two materials lie also in the behavior of their surfaces. The characterization of clean surfaces on the atomic level can be partially done by means of scanning tunneling microscopy (STM), and the results for pure surfaces of Si and Ge are widely documented in literature. For example, Si(111), which is the most frequently studied surface among all Si surfaces, reconstructs in the 7×7 fashion [2], well described in terms of commonly accepted dimeradatom-stacking fault model. In contrast, Ge(111) forms a $c(2 \times 8)$ pattern, in which adatoms are arranged on the T_4 sites of a 1 × 1 surface [3].

No less attention is paid to the interaction of various atomic and molecular species with the surfaces. In particular, interaction of Ni with Si surfaces has attracted a considerable attention due to the richness of phenomena that occur at the interface, especially at elevated temperatures [4-9]. For example, trace amounts of Ni deposited onto the Si(111) can produce significant changes in surface reconstruction patterns, including the formation of the famous $\sqrt{19} \times \sqrt{19}$ superstructure as well as nano-sized islands of nickel silicides [9]. These latter compounds are technologically important because they are frequently integrated in large-scale circuits as ohmic contacts [10]. One of the key concerns is, however, with the NiSi-based contact resistance, which drastically increases with the scaling down of electronic appliances.

The higher mobility of both holes and electrons in Ge compared to those in Si means that metal germanides constitute promising candidates for future high performance semiconductor devices. In search for appropriate materials for electric contacts the interaction of transition metals (TMs) deposited onto germanium surface has been extensively studied [10–17]. It has been reported that Ni films deposited onto Ge surface form a variety

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of Ni_{*x*}Ge_{*y*} phases upon annealing [18, 19]. However, knowledge on the initial stages of Ni interaction with Ge surfaces is rather limited, especially for Ge(111) surface. A combined low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) study has demonstrated that the initial stages of Ni growth on the Ge(111) surface may be described in terms of partial formation of surface compounds [15]. Then, moderate increase in sample temperature promotes a superficial reaction, which results in the formation of the Ni_{*x*}Ge_{*y*} surface compound [20].

In one of our recent study we reported the formation of Ni-containing islands on the Ag/Ge(111)- $\sqrt{3} \times \sqrt{3}$ surface and the Ge(111)-c(2 × 8) surface [21]. In the following, we provide a more detailed description of the changes in the Ni/Ge(111)-c(2 × s8) surface as a function of annealing temperature.

2. Experimental

The sample substrates were cut from commercially available p-type (1 to 10 Ω ·cm resistivity, 500 µm thickness) Ge(111) wafers. After ultrasonic cleaning in acetone the samples were clamped on a molybdenum sample holder and introduced into a UHV chamber. The latter was equipped with a commercial STM (Omicron VT system, base pressure of $\sim 6.0 \times 10^{-9}$ Pa) as well as with a well-collimated e-beam type evaporator for Ni deposition. The sample was prebaked at 800 K (±10 K) overnight. An atomically clean substrate was obtained by cycles of Ar⁺ bombardment $(1.0 \text{ keV}, 10 \text{ to } 90^{\circ} \text{ incidence angle}, 30 \text{ minutes}),$ followed by 1 hour annealing at 1100 K. During sputtering, the sample was kept at RT. After several (usually around 6 to 8) cycles of the cleaning procedure, an STM images showing well-ordered domains of $c(2 \times 8)$ arrangement, were achieved. Then, the Ge(111)-c(2×8) surface, kept at room temperature (RT) was exposed to Ni. The Ni coverage was very roughly estimated with the assumption that 1 ML corresponds to the coverage, at which all atoms of the Ge(111) topmost layer are covered with Ni atoms.

For growth promotion, the surface with deposited material was annealed at three different temperatures: 470 K, 670 K, and 870 K for 30 min. For annealing at elevated temperature resistive mode was used. From our experience, annealing for at least 30 min is necessary to obtain the thermal equilibrium surface. Such a process, whereby a deposit grows after the post-deposition annealing, is known as solid-phase epitaxy in contrast to the so-called reactive epitaxy, in which during deposition the substrate is kept at elevated temperature. The temperature of the substrate below 870 K was measured with K-type thermocouple whereas that above 870 K was read from an optical pyrometer. All STM images presented in this paper were acquired at RT, in a constant-current mode.

3. Results and discussion

Fig. 1 shows a large scale STM image of a clean Ge(111) surface. The surface exhibits terraces separated by single steps. In order to estimate the average step height, we have analyzed a number of STM images acquired under similar tunneling conditions and measured line profiles along the terraces in a manner identical to that shown in Fig. 1. The average step height totals up to 0.27 to 0.31 (±0.01) nm. The obtained value is in a good agreement to the bilayer step height of 0.30 to 0.31 nm, reported by other groups [22, 23]. A high resolution image (bottom inset) confirms that the Ge(111) surface reconstructs in a $c(2 \times 8)$ fashion. In empty state image, a building block of the $c(2 \times 8)$ structure consists of a double-row chain of parallel protrusions (in the inset, an example building block is enclosed by the rectangle). Earlier reports showed that the Ge(111) surface displays a number of disordered boundaries between the neighboring $c(2 \times 8)$ domains, e.g. [1]. Our images support this observation: an example boundary between two $c(2 \times 8)$ domains is shown in the upper inset in Fig. 1).

In an attempt to explore the process of how Ni nucleates and grows on the Ge(111)-c(2×8) surface at RT, we have registered STM images after consecutive depositions. Fig. 2a, which



Fig. 1. STM image of a clean Ge(111)-c(2×8) surface showing three terraces separated by single atomic steps (image size: $100 \times 100 \text{ nm}^2$, bias voltage 1.5 V). Line profile is measured along the line drawn in the image and shows the height of atomic steps.

Upper inset: two c(2 × 8) domains, separated by a boundary (image size: $25 \times 20 \text{ nm}^2$, bias voltage: 1.5 V). Lower inset: a high resolution image of the c(2 × 8) reconstruction on the Ge(111) surface (image size: $10 \times 10 \text{ nm}^2$, bias voltage: 1.5 V). In both insets, building blocks of the c(2 × 8) structure (i.e. double rows) are enclosed by rectangles.

corresponds to a coverage ~ 0.1 monolayer (ML), clearly shows that the initial stages of nucleation is dominated by the formation of threedimensional (3D) clusters with average diameters between 2 and 3 (± 1) nm, distributed inhomogeneously on the surface. The apparent maximum height of the clusters, measured along a straight line drawn in the STM image is $0.15 (\pm 0.01)$ nm (bottom of Fig. 2a). A closer inspection reveals that the boundaries between the neighboring $c(2 \times 8)$ domains, which are typically rich in point defects, serve as predominant nucleation sites for Ni deposition (inset in Fig. 2a). In addition to the domain boundaries, Ni accumulates at defective sites, which are distributed within the terraces. Fig. 2b and 2c show the images of the surface covered by 0.5 ML and 1.2 ML Ni at RT, respectively. We can observe that Ni atoms aggregate to form patches whose shape is irregular in the lateral direction. The line profiles (bottom of Fig. 2b and 2c) show that when the coverage increases, the clusters grow in both lateral and vertical directions. The measured root mean square (RMS) of the roughness of the surface increases with the exposure from 0.05 nm

at 0.1 ML to 0.11 nm at 1.2 ML. The latter value does not differ much from that of a clean Ge(111) surface (RMS_{Ge(111)-c(2 × 8)} = 0.11 nm as measured on flat terraces).



Fig. 2. $80 \times 80 \text{ nm}^2$ empty-state STM images taken after consecutive Ni deposition onto Ge(111)c(2 × 8) surface (top) and typical line profiles measured along lines drawn in the pictures (bottom). The initial Ni coverages are given in the pictures. Inset in (a) shows a zoomed boundary between two neighboring c(2 × 8) domains.

Furthermore, we studied the thermal evolution of the surface evaporated with 0.1 ML Ni. After annealing at 473 K, a range of objects is observable on the surface (some typical examples are shown in Fig. 3a and 3b). We have categorized the objects by their appearance; they are referred as type-1, type-2, and type-3 objects. Type-1 and type-2 objects are both islands with either a $2\sqrt{7} \times 2\sqrt{7}$ or a 3×3 reconstruction at their tops. The islands typically have the height within the range of 0.15 to 0.20 nm (Fig. 3c), and adopt approximately triangular or trapezoidal shapes. However, a few islands are observed with irregular shapes. In contrast, the type-3 objects have hexagonal shapes and are much higher (typical height totals up to 0.45 to $0.55 (\pm 0.01)$ nm) and do not form distinct reconstruction patterns at their tops (Fig. 3d). The type-3 objects are observed at lower densities as compared to their above mentioned counterparts.

In the area between the islands, the $c(2 \times 8)$ reconstruction is fully retained. However, an inspection of the substrate surface reveals the occurrence of ring-like features, which have not existed on either the clean surface or the surface covered



Fig. 3. STM images showing the evolution of the Ge(111)- $c(2 \times 8)$ surface covered with 0.1 ML Ni after annealing at 473 K: (a) large scale image: three types of islands (described in the text) are highlighted by circles. Inset shows the area enclosed with a Box, (b) top: image showing a depression within the $c(2 \times 8)$ terrace; bottom: line profile measured along a depression in the terrace, (c) top: small scale image of type-1 and type-2 islands; bottom: line profile measured along the line shown in the image, (d) top: small scale image of type-3 island; bottom: line profile along the line in the image.

The image size and bias polarity are as follows: (a) $80 \times 80 \text{ nm}^2$, 1.7 V; (b) $40 \times 40 \text{ nm}^2$, 1.3 V; (c) $25 \times 45 \text{ nm}^2$, 1.9 V; (d) $16 \times 12 \text{ nm}^2$, 1.6 V.

by Ni atoms at RT. Therefore, we presume that the features must be due to Ni interaction with the Ge(111) surface at elevated temperature. The features typically emerge in a single, dimer or trimer configuration (in Fig. 3a, the exemplary rings are shown in the inset).

By comparing Fig. 3a with the large scale image of the clean Ge(111)-c(2×8) surface (Fig. 1) we can notice a significant difference in the shape of the edge separating the terraces. From this we can infer that the process to form islands involves a considerable Ge atoms consumption from the terrace edges. In Fig. 3b, which is taken from another region of the same substrate surface than the one shown in Fig. 3a, we can notice a depression in the terrace. The depth of the depression, measured with the line profile (bottom of Fig. 3b) corresponds to a single terrace height of a not modified Ge(111) surface. Since such depressions have not been observed on the clean surface we suspect that their occurrence here is caused by Ge consumption from this area. Therefore, we postulate that Ge consumption occurs not only at the terrace edges but also from the terraces.

After annealing the surface at 673 K, the type-3 islands grow laterally at the cost of a complete disappearance of both the type-1 and the type-2 islands (Fig. 4). Upon analyzing a number of large-scale STM images we have found that the islands size is between 7 and 22 (±1) nm in diameter, and 0.38 to 0.50 (±0.1) nm in height. Statistical distribution of the islands height is shown in Fig. 4. We have estimated that the islands volume makes up roughly half of the Ni clusters volume deposited on the surface (e.g, for a randomly chosen $120 \times 120 \text{ nm}^2$ image, taken after annealing at 673 K, the total volume of the islands amounts to 652 nm³, while the total volume of Ni clusters evaporated on the same surface is 1380 nm^3). The observed decrease in volume could be due to Ni diffusion into the Ge(111) bulk, deposit reevaporation or stoichiometric changes. It is noteworthy that unlike the islands lateral dimension, which changes over a relatively wide range, their vertical dimension is almost fixed. In the area between the islands, the $c(2 \times 8)$ reconstruction of the substrate is retained, and the ring-like structures are still observed (upper inset in Fig. 4).

Annealing at 873 K seems to be powerful enough to cause the degradation of the islands (Fig. 5). Also, the ring-like objects are not seen. Instead, a number of irregular patches develop on the terraces. We propose that the patches represent remains of the islands. The quality of the surface is much worse as compared to those presented in the above discussed images, due to the abundance of defects.



Fig. 4. Top: STM image $(80 \times 80 \text{ nm}^2, \text{ bias voltage:} 1.5 \text{ V})$ showing hexagonal islands formed on the Ge(111)-c(2 × 8) surface evaporated with 0.1 ML Ni after annealing at 673 K. Upper inset shows the area $(30 \times 20 \text{ nm}^2)$ enclosed with a box. Bottom inset presents cross-section measured along the line shown in the image. Bottom inset shows distribution as a function of islands height.

We presume that all types of islands discussed in the present paper belong to Ni_xGe_y surface compounds. We shall recall that at around 320 K, the reaction of thin Ni film deposited onto Ge surface results in simultaneous growth of both Ni₅Ge₃ and NiGe [18]. Furthermore, annealing of 10 nm-thick Ni layer on Ge(111) at 673 K leads to the formation of NiGe and Ni₃Ge₂ [19]. Therefore, we speculate that the type-3 islands might belong to NiGe



Fig. 5. $80 \times 80 \text{ nm}^2$ STM image showing the evolution of the Ge(111)-c(2 × 8) surface covered with 0.1 ML Ni after annealing at 873 K (bias voltage: 1.5 V). Irregular bright-imaged patches are seen on strongly defected surface.

phase since they are observed in STM images taken after annealing at 473 K and then at 673 K. The type-1 and type-2 islands might represent Ni₅Ge₃ phase. However, our assumption is rather speculative. It has been demonstrated that upon annealing at 873 K, a uniform nickel germanide film breaks into discrete islands [20]. Instead, for small Ni coverages we have recorded a complete decomposition of Ni_xGe_y islands.

One may think of the origin of the ring-like features, which are observed in coexistence with the islands. Although at first glance they resemble missing Ge atoms, dual-polarity images taken over the same scanning area (Fig. 6) shed more light on their origin. Namely, we can readily notice that while in the empty state image the features appear as dark rings (Fig. 6a), in the filled state image (Fig. 6b) they are even brighter in contrast to Ge atoms, meaning that they are more likely to represent Ni atoms situated on top of Ge atoms rather than missing Ge atoms.

We would like to recall that the occurrence of ring-like objects was commonly observed after



Fig. 6. $38 \times 20 \text{ nm}^2$ empty-state (a) and filled-state (b) STM images of the same area, which were grown under the same conditions as the surface shown in Fig. 3. Exemplary ring-like objects are enclosed by solid circles. Bias volatge is: 1.5 V (a) and -0.7 (b).

deposition of small TMs onto Si(111) surface. For example, the appearance of isolated rings on the Ni/Si(111) surface was ascribed to the precursors to Ni-induced Si(111)- $\sqrt{19} \times \sqrt{19}$ surface reconstruction. Wawro et al. noticed the formation of ring-like structures when 0.33 ML Fe deposited onto Si(111) surface was annealed at 523 K [24]. A close resemblance between the observed rings and the building elements of a 2×2 reconstruction, which develops on tops of iron silicide islands has led the authors to conclude that the rings constitute a very initial formation stage of iron silicide. The occurrence of ring-like clusters has been also reported when 0.25 ML Co, deposited onto Si(111) surface at 373 K was then annealed to 943 K, and interpreted in terms of the formation of an intermediate stage between the clean and silicide-Si interface [25]. Finally, we would like to underline that the appearance of ring-like features has not been reported for the Co/Ge(111) surface [16].

4. Conclusion

We have reported STM images to illustrate thermally-induced evolution of the morphology of Ni/Ge(111)-c(2 × 8) surface. We have found that at room temperature, the nucleation proceeds inhomogeneously, and the boundaries between different c(2 × 8) domains are particularly active for Ni reaction with the surface. Annealing within 473 to 673 K temperature range results in the formation of Ni_xGe_y islands on the Ge(111)-c(2 × 8) matrix. The process to form islands involves Ge atom consumption from both terrace edges and simply from the terraces. Unlike for the Co/Ge(111) surface system, Ni interaction with the Ge(111) surface results in the formation of relatively stable ring-like features, in which Ni atoms are adsorbed on tops of Ge atoms. The islands are stable at temperatures lower than 873 K, at which they undergo a thermal degradation.

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References

- RUSSEL B., Semiconductor Surfaces: Germanium, in: STROSCIO J.A., KAISER W.J. (Eds.), Scanning Tunneling Microscopy, Academic Press, San Diego, 1993, p. 225.
- [2] TAKAYANAGI K., TARISHIRO Y., TAKAHASHI S., TAKAHASI M., *Surf. Sci.*, 164 (1985), 367.
- [3] BECKER R.S., SWARTZENTRUBER B.S., VICKERS J.S., KLITSNER T., *Phys. Rev. B*, 39 (1989), 1633.
- [4] BISI O., CHIAO L.W., TU K.N., Phys. Rev. B, 30 (1984), 4664.
- [5] MANGELINCK D., GAS P., GROB A., PICHAUD P., THOMAS O., J. Appl. Phys., 79 (1996), 4078.
- [6] GUO X., YU H., JIANG Y.L., RU G.P., ZHANG D.W., LI B.Z., Appl. Surf. Sci., 257 (2011), 10571.
- [7] KINODA G., OGAWA K., Surf. Sci., 461 (2000), 67.
- [8] KOCZOROWSKI W., BAZARNIK M., CZAJKA R., Acta Phys. Pol. A, 120 (2011), 480.
- [9] YOSHIMURA M., SHINABE S., YAO T., Surf. Sci., 357 358 (1996), 917.
- [10] CHAWANDA A., NYAMHERE C., AURET F.D., MTANGI W., DIALE M., NEL J.M., *Phys. Status Solidi C*, 7 (2) (2010), 248.
- [11] TSUI F., HE L., MA L., TKACHUK A., CHU Y.S., NAKAJIMA K., CHIKYOW T., *Phys. Rev. Lett.*, 91 (2003), 177203.
- [12] MOCKING T.F., HLAWACEK G., ZANDVLIET H.J.W., Surf. Sci., 606 (2012), 924.
- [13] SELL K., KLEIBERT A., OEYNHAUSEN V.V., MEIWES-BROER K.H., *Eur. Phys. J. D.*, 45 (2007), 433.
- [14] CHOI J., LIM D.K., KIM Y., KIM S., J. Phys. Chem. C, 114 (2010), 8992.
- [15] GIRARDEAUX C., TÔKEI Z., CLUGNET G., ROLLAND A., Appl. Surf. Sci., 162 (2000), 208.
- [16] MOCKING T.F., POELSENA B., ZANDVLIET H.J.W., Surf. Sci., 610 (2013), 59.
- [17] GRZELA T., KOCZOROWSKI W., CAPELLINI G., CZA-JKA R., RADNY M.W., CURSON N., SCHOFIELD S.R., SCHUBERT M.A., SCHROEDER T., J. Appl. Phys., 115 (2014), 074307.

- [18] PERRIN C., MANGELINCK D., NEMOUCHI F., LABOR J., LAVOIE C., BERGMAN C., GAS P., *Mat. Sci. Eng. B-Adv.*, 154 – 155 (2008), 163.
- [19] JIN L.J., PEY K.L., CHOI W.K., FITZGERALD E.A., ANTONIADIS D.A., PITERA A.J., LEE M.L., CHI D.Z., TUNG C.H., *Thin Solid Films*, 462 – 463 (2004) 151.
- [20] ZHANG Q., WU N., OSIPOWICZ T., BERA L.K., ZHU C., Jpn. J. Appl. Phys., 44 (2005), L1389.
- [21] FU T.Y., TOMASZEWSKA A., HUANG X.L, LI J.H., HSIEH P.I., JHOU M.K., Nanoscale Res. Lett., 8 (2013), 416.
- [22] WINTTERLIN J., AVOURIS P., J. Chem. Phys., 100 (1994), 687.
- [23] GOETHELID M., BJOERKQVIST M., KARLSSON U.O., FLODSTRÖM, *Microsc. Microanal. Microstruct.*, 5 (1994), 277.
- [24] WAWRO A., SUTO S., CZAJKA R., KASUYA A., Phys. Rev. B, 67 (2003), 195401.
- [25] BENNETT P.A., PARIKH S.A., CAHILL D.G., J. Vac. Sci. Technol. A, 11 (1993), 1680.

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