

## Initial stage of Ag growth on Si(001) studied by high-resolution Rutherford-backscattering spectroscopy

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 (Received 24 March 1995)

The initial stage of Ag growth on the Si(001) $2\times 1$  surface is observed at 520 and 760 K by monolayer-resolvable high-resolution Rutherford-backscattering spectroscopy. At 760 K, the coverage of Ag saturates at 0.5 ML. (1 ML =  $6.78\times 10^{14}$  atoms/cm<sup>2</sup>) after formation of a two-dimensional Ag layer. The position of the Ag atom is determined from observed inelastic energy losses of He ions scattered from the Ag atoms. The growth mode at 520 K is found to be the Stranski-Krastanov mode with a critical thickness of 0.5 ML for the initial layer growth.

### I. INTRODUCTION

In recent years, various metal/silicon systems have been studied for better understanding of the interface properties such as Schottky barrier formation, contact resistance, thin-film adhesion, etc.<sup>1</sup> One of the most interesting systems is Ag/Si because it is a very nonreactive metal/silicon system. Unlike the Ag/Si(111) system, which has been extensively studied, there have been a relatively small number of studies on the Ag/Si(001) system.<sup>2-11</sup> Although it is confirmed that the growth of Ag on Si(001) is Stranski-Krastanov (SK) mode, there is controversy on the critical thickness for the initial layer growth. The observed critical thicknesses range from 0.27 to 1.5 ML.<sup>4,6,9,10</sup> The disagreement over the critical thickness is in part attributed to the lack of information about the absolute Ag coverage, which is difficult to measure with conventional techniques such as ion scattering spectroscopy, Auger electron spectroscopy, etc.

Rutherford-backscattering spectroscopy (RBS) has been widely used in analysis of solids.<sup>12</sup> Although it allows quantitative and nondestructive analysis, the depth resolution (typically  $\sim 10$  nm) is not good enough for surface analysis. Recently, we have demonstrated that monolayer resolution can be achieved in RBS using a high-resolution spectrometer and a grazing angle technique.<sup>13</sup> This technique, called *high-resolution Rutherford-backscattering spectroscopy* (HRBS), realizes quantitative layer-by-layer analysis without destruction of specimens. Such analysis cannot be performed by other conventional techniques.

We have shown that HRBS is a powerful tool in the study of epitaxial growth.<sup>14</sup> Figure 1 shows typical growth modes, Frank-van der Merwe mode (FM mode) and Volmer-Weber mode (VW mode). The HRBS spectra in these growth crystals are also shown schematically. In the FM mode, atomic layers of the growth crystal can be resolved as separated peaks in the HRBS spectrum. On the other hand, in the VW mode, energies of ions scattered from the same atomic layer are not always the same. For example, the energy of a scattered ion *B* shown in Fig. 1(b) is smaller than that of *C* because the

path length of *B* is longer than that of *C*. Consequently, the HRBS spectrum does not show separated peaks but shows a broad peak as shown schematically in Fig. 1(b). Thus the growth mode can be easily determined by HRBS measurement.

The usefulness of HRBS for the study of epitaxial growth is demonstrated in Fig. 2. Shown are examples of the HRBS spectra observed during the initial stage of PbTe growth on SnTe(001). There are several peaks in the spectra, at  $\sim 285.6$ ,  $\sim 283.4$ , and  $\sim 281$  keV. These peaks correspond to He ions scattered by Pb atoms in the first, second, and third atomic layers of the PbTe overgrown on the SnTe(001). These spectra indicate that the growth mode is basically the FM mode.<sup>14</sup> In the present paper, we report an application of HRBS to the study of the initial stage of the Ag growth on a Si(001) surface.

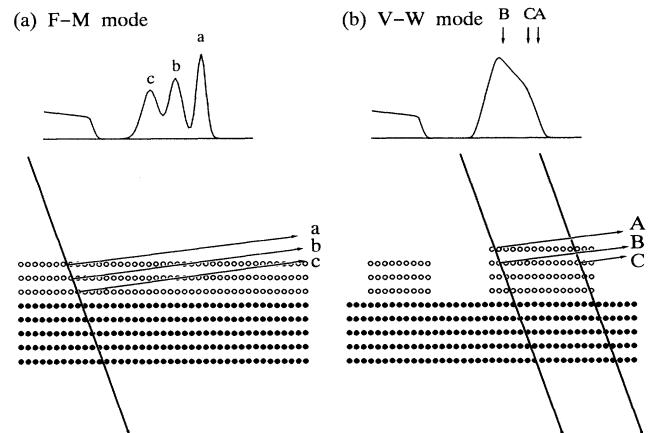


FIG. 1. Typical growth modes: (a) FM mode and (b) VW mode. Solid circles show the substrate atoms and open circles show the growth atoms. Energy spectra expected from these growth modes are also shown schematically. The growth mode can be easily determined by HRBS.

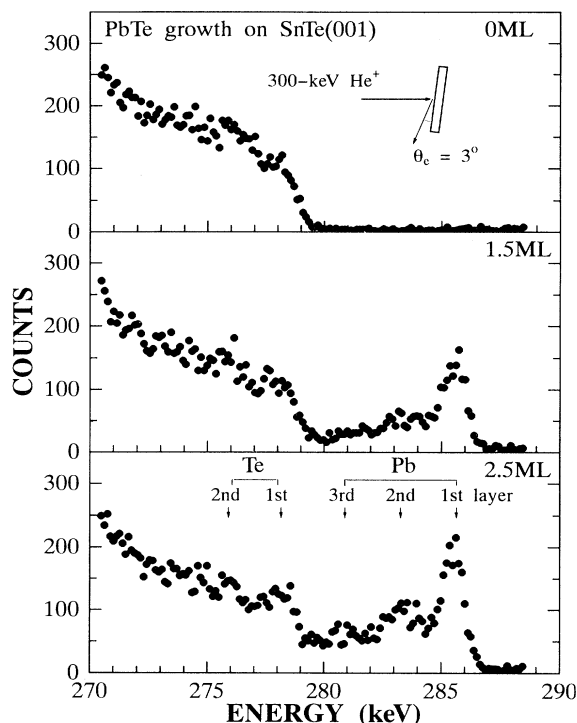


FIG. 2. Examples of the HRBS spectra observed by 300-keV  $\text{He}^+$  ions during the growth of PbTe on SnTe(001) at 400 K. The scattering angle is  $100^\circ$  and the exit angle is  $3^\circ$  measured from the surface plane. Peaks at  $\sim 285.6$ ,  $\sim 283.4$ , and  $\sim 281$  keV correspond to the Pb atoms in the first, second, and third PbTe layers overgrown on the SnTe(001). These spectra show that the growth mode is basically the FM mode.

## II. EXPERIMENT

The measurement of HRBS was performed in an UHV scattering chamber (base pressure  $3 \times 10^{-10}$  Torr), which was connected to a 4-MV Van de Graaff accelerator via a differential pumping system. An oxidized  $n$ -type Si(001) wafer was mounted on a high-precision goniometer. A clean Si(001) surface was prepared by the dc-resistive heating of the wafer at about 1100 K. The surface showed a  $2 \times 1$  reflection high-energy electron diffraction (RHEED) pattern. Silver was deposited on the surface by evaporation from a tungsten filament at a rate about 0.5 ML/min [1 ML =  $6.78 \times 10^{14}$  atoms/cm<sup>2</sup>, the density of the Si(001)  $1 \times 1$  surface]. The deposition rate was measured by a quartz microbalance calibrated by RBS.

A beam of 300-keV  $\text{He}^+$  ions from the Van de Graaff accelerator was collimated to  $2.5 \times 2.5$  mm<sup>2</sup> by a series of apertures. The beam current, typically about 5 nA, was monitored by a vibrating beam chopper. The ions scattered from the Ag/Si(001) surface at  $65^\circ$  were energy analyzed by a  $90^\circ$  sector magnetic spectrometer. The acceptance angle of the spectrometer was  $1.6 \times 10^{-4}$  Sr. The energy window was 9% and the energy resolution was about 0.1% including the energy spread of the incident ion beam. A typical dose for one HRBS measurement was about  $5 \mu\text{C}$ . The energy spectra were measured with various Ag coverages. In order to avoid the radiation

damage, the surface was cleaned up by heating at 1000 K after each HRBS measurement and different amount of Ag was deposited on the clean surface before a new HRBS measurement.

## III. RESULT

Figure 3 shows examples of the observed energy spectra of  $\text{He}^+$  ions scattered at  $65^\circ$  from the Ag/Si(001) surfaces with various amounts of Ag deposition at 760 K. The exit angle  $\theta_e$  measured from the surface plane was  $3^\circ$ , and the azimuthal angle of the specimen was carefully chosen in order to avoid channeling and blocking effects. There is a sharp peak at about 287 keV, which corresponds to ions scattered from adsorbed Ag atoms. The ions scattered from Si atoms ( $< 254$  keV) are not shown. The full width at half maximum of the peak is about 1 keV irrespective of the Ag coverage, which corresponds to a depth of 0.1 nm. This indicates a formation of a two-dimensional Ag layer. The surface was also examined during the growth by RHEED. The  $2 \times 1$  RHEED pattern was seen even after deposition of 5-ML Ag.

Figure 4 shows examples of the observed energy spectra of  $\text{He}^+$  ions scattered from the Ag/Si(001) surfaces with various amounts of Ag deposition at 520 K. Experi-

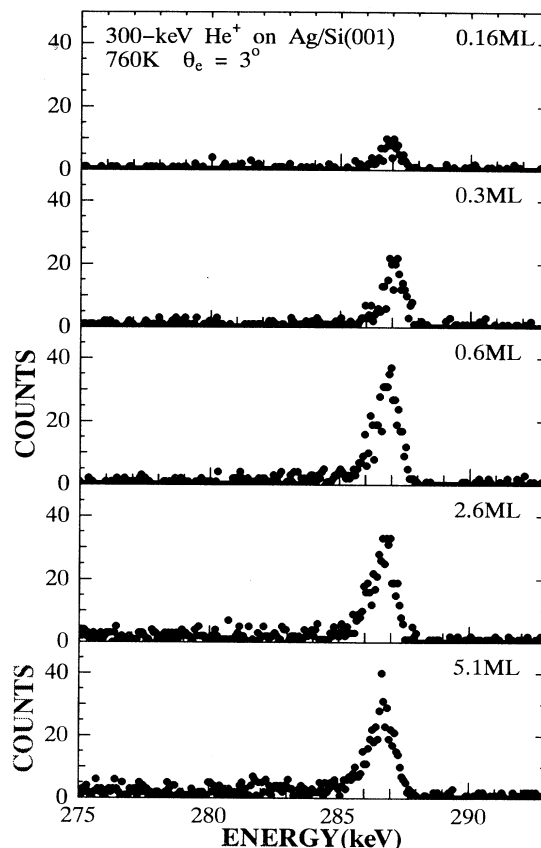


FIG. 3. Examples of the HRBS spectra observed at  $\theta_e = 3^\circ$  during the growth of Ag/Si(001) at 760 K. There is a sharp peak corresponding to two-dimensional Ag layer.

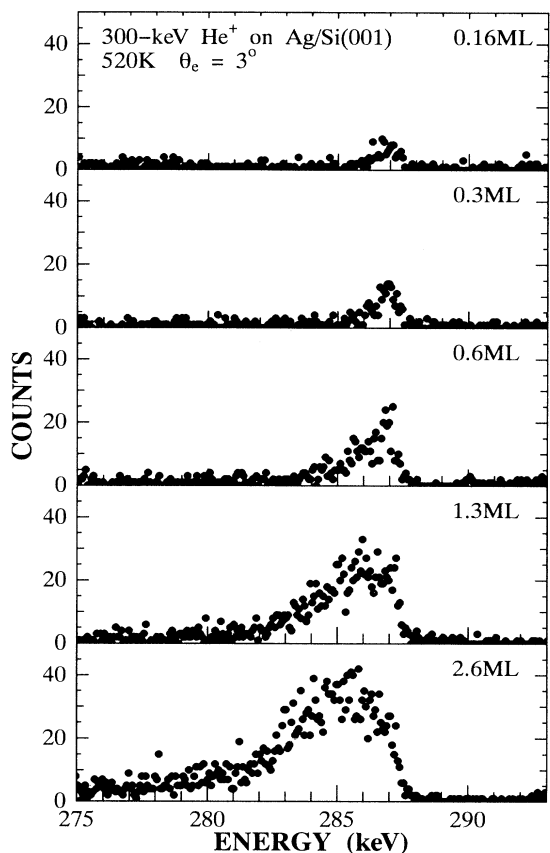


FIG. 4. Examples of the HRBS spectra observed at  $\theta_e = 3^\circ$  during the growth of Ag/Si(001) at 520 K. The spectra show that the growth mode is the SK mode with a critical thickness of about 0.5 ML for the initial layer growth.

mental conditions were the same as those in Fig. 3 except for the substrate temperature. At the beginning of the growth, the spectrum shows the same features as observed at 760 K, i.e., Ag atoms form a two-dimensional layer. Different from the deposition at 760 K, the peak has a tail in the low energy side at the deposition of 0.6 ML. The tail becomes larger with deposition and finally the spectrum shows a broad peak. The surface showed the  $2 \times 1$  RHEED pattern at the beginning of the growth. With increasing deposition, the  $2 \times 1$  RHEED pattern became weaker and reflection spots from the Ag single crystal appeared. The orientation relationship between the Ag crystal and the substrate Si was

$$(001)_{\text{Ag}} \parallel (001)_{\text{Si}}, [100]_{\text{Ag}} \parallel [100]_{\text{Si}}.$$

This relationship is the same one that was observed by RHEED at room temperature.<sup>10</sup>

#### IV. DISCUSSION

##### A. Growth at 760 K

Figure 5 shows the observed ion yield from Ag atoms as a function of the amount of Ag deposition. While the yield increased linearly with deposition at 520 K, yield

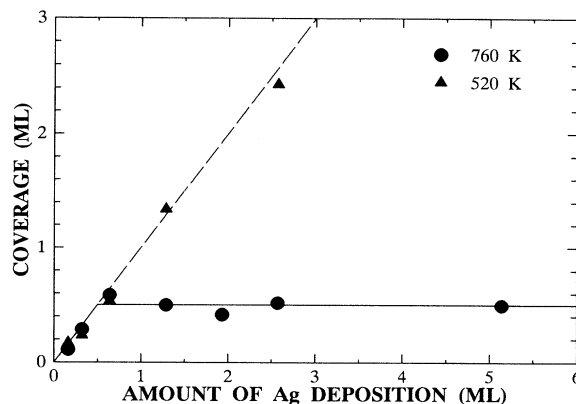


FIG. 5. Coverage of Ag as a function of the Ag deposition. While the coverage increases linearly with increasing deposition at 520 K, the saturation of the coverage is observed at 760 K.

saturation was observed at 760 K. The diffusion coefficient of Ag in Si at 760 K is estimated to be  $5 \times 10^{-14}$  cm<sup>2</sup>/sec from the high-temperature data.<sup>15</sup> The high diffusibility suggests that the excess Ag diffuses into the bulk.

The initial stage of Ag deposition on Si(001) at room temperature was observed by scanning-tunneling microscopy.<sup>6</sup> It was found that Ag atoms adsorb at twofold bridge sites in between adjacent Si dimmer rows (see Fig. 7). The expected saturation coverage for this adsorption site is 0.5 ML, showing good agreement with the present saturation coverage observed at 760 K. This agreement and the observed  $2 \times 1$  RHEED pattern suggest that the adsorption site at 760 K is also the twofold bridge site.

The peak energy of the spectrum shown in Fig. 3 is slightly smaller than the energy of He ions elastically scattered from Ag atoms (287.4 keV). The energy difference is ascribed to the inelastic energy loss.<sup>16</sup> Be-

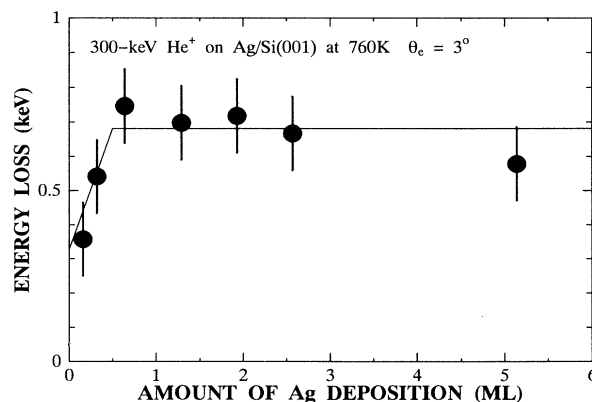


FIG. 6. Change of the inelastic energy loss of He<sup>+</sup> ions scattered from Ag atoms during the growth of Ag/Si(001) at 760 K. The energy loss increases with increasing deposition at the beginning and becomes almost constant after deposition of 0.5 ML. The line indicates the calculated result with a model discussed in the text.

cause the energy loss depends on the position of the Ag atom from which the ion is scattered, the Ag position can be determined from the observed energy loss. As the observed inelastic energy loss is very small, special care was taken on the possible fluctuation of the incident-beam energy. We measured HRBS spectra at  $\theta_e = 3^\circ$  and  $15^\circ$  alternately to correct the fluctuation of the incident-beam

energy. By this procedure, the energy difference between the mean energies of the Ag peaks at  $\theta_e = 3^\circ$  and  $15^\circ$ ,  $\langle E(15^\circ) \rangle - \langle E(3^\circ) \rangle$ , can be determined precisely. The inelastic energy loss is proportional to  $(1/\sin\theta_i + 1/\sin\theta_e)$ , as will be seen in Eqs. (2) and (3), where  $\theta_i$  is the incident angle measured from the surface plane. Therefore the inelastic energy loss at  $\theta_e = 3^\circ$  is given by

$$\Delta E(3^\circ) = \{ \langle E(15^\circ) \rangle - \langle E(3^\circ) \rangle \} \frac{\frac{1}{\sin(62^\circ)} + \frac{1}{\sin(3^\circ)}}{\left\{ \frac{1}{\sin(62^\circ)} + \frac{1}{\sin(3^\circ)} \right\} - \left\{ \frac{1}{\sin(50^\circ)} + \frac{1}{\sin(15^\circ)} \right\}} . \quad (1)$$

Figure 6 shows the inelastic energy loss observed at 760 K as a function of the amount of Ag deposition. The energy loss increases with Ag deposition and becomes constant ( $680 \pm 80$  eV), within the experimental error, after the deposition of 5 ML.

Figure 7 schematically shows the scattering of a He ion from an adsorbed Ag atom. The energy loss consists of two contributions: one is the contribution of the adsorbed Ag atoms and the other is the contribution of the Si(001) surface. The energy loss due to the adsorbed Ag atoms is given by

$$\Delta E_{\text{Ag}} = \frac{\sigma_{\text{Ag}} n_{\text{Ag}}}{2} \left( \frac{1}{\sin\theta_i} + \frac{1}{\sin\theta_e} \right) , \quad (2)$$

where  $n_{\text{Ag}}$  is the density of the adsorbed Ag atoms,  $\sigma_{\text{Ag}}$  is the stopping cross section of Ag, and the straight-line approximation is employed for the ion trajectory. The increase of the observed energy loss at the deposition  $< 0.5$  ML is ascribed to the increase of  $n_{\text{Ag}}$ .

The energy loss due to adsorbed Ag atoms is calculated to be 297 eV at the coverage of 0.5 ML using  $\sigma_{\text{Ag}} = 8.65 \times 10^{-14}$  eV cm<sup>2</sup>,<sup>17</sup>  $n_{\text{Ag}} = 3.39 \times 10^{14}$  atoms/cm<sup>2</sup>,  $\theta_i = 62^\circ$ , and  $\theta_e = 3^\circ$ . The difference between the observed energy loss ( $680 \pm 80$  eV) and the calculated Ag contribution is  $380 \pm 80$  eV. This corresponds to the contribution of the Si(001) surface, which is written as

$$\Delta E_{\text{Si}} = \left( \frac{1}{\sin\theta_i} + \frac{1}{\sin\theta_e} \right) \int_{x_a}^{\infty} S(x) dx , \quad (3)$$

where  $S(x)$  is the stopping power at a distance  $x$  from the surface, and  $x_a$  is the height of the adsorbed Ag atom on the surface (see Fig. 7). The surface stopping power consists of two parts, plasmon excitation and single electron collision.<sup>18,19</sup> The stopping power due to plasmon excitation is given by<sup>20</sup>

$$S_{\text{pl}}(x) = \left( \frac{Ze\omega_p}{v} \right)^2 \left[ \ln \left( \frac{[q_0^2 - (\omega_p/v)^2]^{1/2} + q_0}{\omega_p/v} \right) \theta(-x + x_e) + \frac{x - x_e}{|x - x_e|} \int_0^{\{q_0^2 - (\omega_p/v)^2\}^{1/2}} dq \frac{\exp\{-2|x - x_e|[q^2 + (\omega_p/v)^2]^{1/2}\}}{\{q^2 + (\omega_p/v)^2\}^{1/2}} \right] , \quad (4)$$

where  $Ze$  is the ion charge,  $\omega_p$  is the plasmon frequency,  $v$  is the ion velocity,  $q_0$  is the cutoff wave number, and  $x_e$  is the position of the electron surface which is assumed to be one-half of the interplanar distance.<sup>20</sup> The binary encounter model gives the stopping power due to the single electron collisions as<sup>19</sup>

$$S_{\text{s.e.}}(x) = \left( \frac{Ze\omega(x)}{v} \right)^2 \ln \left[ \frac{2m v^2}{\hbar\omega(x)} \right] , \quad (5)$$

where  $m$  is the electron mass,  $\omega(x) = [4\pi e^2 n(x)/m]^{1/2}$ , and  $n(x)$  is the electron density. The sum of these for-

mulas explained the observed energy losses of the specularly reflected ions from single-crystal surfaces quite well.<sup>18,19</sup> Substituting the sum of these formulas into Eq. (3), the energy loss can be calculated. The calculated total energy loss is shown as a function of  $x_a$  in Fig. 8. In the calculation of  $S(x)$ , the Si(001) surface was assumed to be a truncated bulk surface. Comparing the calculated result with the experimental result,  $680 \pm 80$  eV, the height of the adsorbed Ag atoms,  $x_a$ , is determined to be  $5 \pm 10$  pm.

## B. Growth at 520 K

The spectrum observed at 520 K is almost the same as that at 760 K in the beginning of the growth. This indi-

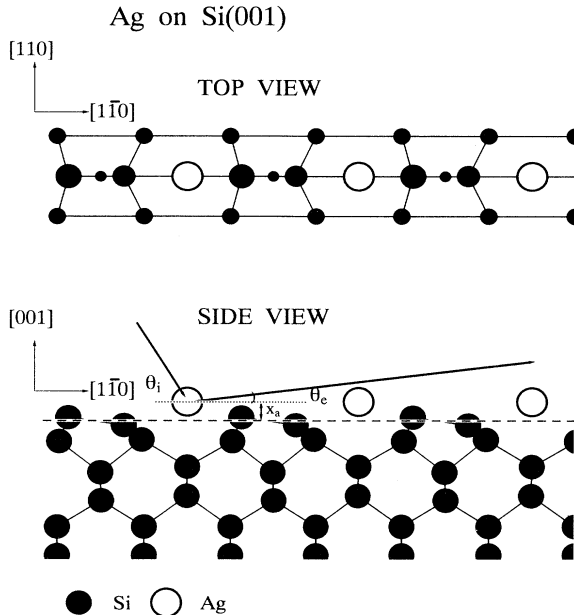


FIG. 7. Ag adsorption site suggested by scanning tunnel microscope observation. Scattering of He ions from Ag atoms adsorbed on the Si(001) is also shown. Although the configuration of Si atoms shown in the figure is that of the Si(001)  $2 \times 1$  surface, Si atoms might rearrange due to the adsorption of Ag atoms.

cates that Ag formed a two-dimensional layer until the coverage of  $\sim 0.5$  ML. At the deposition of more than 0.5 ML, the spectrum shows a tail in the low-energy side. The tail becomes larger with increasing deposition. The spectrum does not show well-defined peaks corresponding to successive atomic layers like the spectrum in Fig. 2 [the expected peak spacing is 2.1 keV for the Ag(001) surface]. This suggests that small islands grow after the formation of the two-dimensional Ag layer of about 0.5 ML thick, i.e., the growth mode is the SK mode with the critical thickness of 0.5 ML.

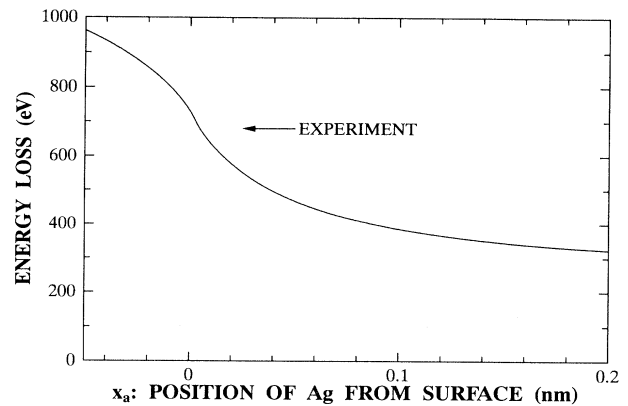


FIG. 8. Calculated energy loss of the He ions scattered from adsorbed Ag atoms as a function of the height of the Ag atoms,  $x_a$ . Comparing with the observed energy loss,  $680 \pm 80$  eV,  $x_a$  is determined to be  $5 \pm 10$  pm.

## V. CONCLUSION

The initial stage of Ag growth on the Si(001) $2 \times 1$  surface is observed by HRBS at 760 and 520 K. The formation of a two-dimensional Ag layer is observed at the beginning of the growth. At 760 K, the coverage of the Ag layer saturates at 0.5 ML (1 ML =  $6.78 \times 10^{14}$  atoms/cm<sup>2</sup>). The height of the adsorption site is determined to be  $5 \pm 10$  pm from the observed inelastic energy loss. On the other hand, at 520 K, formation of small islands is observed after the two-dimensional layer growth, i.e., the growth mode is the Stranski-Krastanov mode. The critical thickness for the initial layer growth is 0.5 ML.

## ACKNOWLEDGMENTS

We are grateful to the members of the Department of Nuclear Engineering of Kyoto University for use of the 4-MV Van de Graaff accelerator. One of us (K.K.) is grateful to the Shimazu Science Foundation for financial support. This study was supported in part by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science and Culture.

<sup>1</sup>A. Hiraki, *Surf. Sci.* **168**, 74 (1986).

<sup>2</sup>T. Hanawa and K. Oura, *Jpn. J. Appl. Phys.* **16**, 519 (1977).

<sup>3</sup>M. Hanbücken and H. Neddermeyer, *Surf. Sci.* **114**, 563 (1982).

<sup>4</sup>M. Hanbücken, M. Futamoto, and J. A. Venables, *Surf. Sci.* **147**, 433 (1984).

<sup>5</sup>A. Samsaver, T. Miller, and T.-C. Chiang, *Phys. Rev. B* **38**, 9889 (1988).

<sup>6</sup>A. Samsaver, E. S. Hirschorn, F. M. Leibsle, and T.-C. Chiang, *Phys. Rev. Lett.* **63**, 2830 (1989).

<sup>7</sup>T. Hashizume, R. J. Hamers, J. E. Demuth, K. Markert, and T. Sakurai, *J. Vac. Sci. Technol. A* **8**, 249 (1990).

<sup>8</sup>A. Brodde, D. Badt, St. Tosch, and H. Neddermeyer, *J. Vac. Sci. Technol. A* **8**, 251 (1990).

<sup>9</sup>K. Nishimori, H. Tokutaka, T. Tamon, S. Kishida, and N. Ishihara, *Surf. Sci.* **242**, 157 (1991).

<sup>10</sup>Y. Kimura and K. Takayanagi, *Surf. Sci.* **276**, 166 (1992).

<sup>11</sup>Y. Borenstein and R. Alameh, *Appl. Surf. Sci.* **65/66**, 735 (1993).

<sup>12</sup>For example, L. C. Feldman and J. W. Mayer, *Fundamentals of Surfaces and Thin Film Analysis* (North-Holland, Amsterdam, 1986), Chap. 3.

<sup>13</sup>K. Kimura, K. Ohshima, and M. Mannami, *Appl. Phys. Lett.* **64**, 2232 (1994).

<sup>14</sup>K. Kimura, K. Ohshima, and M. Mannami, in *Proceedings of the 3rd IUMRS International Conference on Advanced Materials, Tokyo, 1993*, edited by H. Sakaki *et al.* (Elsevier, Amsterdam, 1994).

<sup>15</sup>B. I. Boltaks and Hsüeh Shih-yin, *Fiz. Tverd. Tela (Leningrad)* **2**, 2677 (1960) [*Sov. Phys. Solid State* **2**, 2383 (1961)].

<sup>16</sup>K. Kimura, H. Ohtsuka, K. Ohshima, and M. Mannami,

- Nucl. Instrum. Methods Phys. Res. Sect. B **90**, 227 (1994).
- <sup>17</sup>H. H. Andersen and J. F. Ziegler, *The Stopping and Ranges of Ions in Matter* (Pergamon, New York, 1977).
- <sup>18</sup>K. Kimura, M. Hasegawa, and M. Mannami, Phys. Rev. B **36**, 7 (1987).
- <sup>19</sup>Y. Fujii, S. Fujiwara, K. Narumi, K. Kimura, and M. Mannami, Surf. Sci. **277**, 164 (1992).
- <sup>20</sup>R. Kawai, N. Itoh, and Y. H. Ohtsuki, Surf. Sci. **114**, 647 (1976).