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FOOTPRINT OF SILICON CLUSTERS IN MBE-GROWN EPI-LAYERS ON SILICON WAFERS

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ABSTRACT

The participation of small clusters in the growth of perfect crystalline thin films, as e.g. by molecular beam epitaxy, is now a generally accepted phenomenon in spite of the atomic nature of incorporation into a one-layer-at-a-time two-dimensional growth process. There is no reason, that in general a cluster formed with more than three atoms, adopts a two-dimensional appearance. This suggests that clusters do not incorporate in a crystal surface without changes of their inner bonding. Nevertheless is the question, whether a cluster adopts itself to the plane growing surface, maintaining more or less the original neighborhood of atoms, or it decays completely into single atoms, which now acquire mobility and independence from each other, is still unanswered. We propose a model and an experimental technique, which should help to clarify this question. Indeed is the knowledge of these processes important for the controlled deposition at high growth rate of perfect crystalline thin films. It might also shed light on the topic of the existence and efficiency of a near-surface transition layer in front of a growing film, where the mobility of incorporating species is supposed to be high. The most direct way of marking the atoms in a cluster might be by use of isotopes, which do not interfere with the physics and chemistry of crystal formation. Nuclear magnetic resonance (NMR) is a sensitive tool for the detection of nuclear paramagnetism, which is related to a net nuclear spin present in a number of atoms. We discuss the application of ^{28}Si- and ^{29}Si-isotopes in clusters, where a difference of spin-spin coupling and consequently of NMR-signals occurs for ^{29}Si-atoms surrounded by either (unmagnetic) ^{28}Si-atoms, or ^{29}Si-atoms surrounded by the same (magnetic) species on top of the growing film.

KEYWORDS: Clusters, MBE, NMR, Silicon, capas delgadas

1. INTRODUCTION

Homoepitaxial growth of silicon on Si(111) and Si(100) surfaces by molecular beam epitaxy (MBE) has been intensively studied for more than two decades [1-4]. It has been shown, that MBE-growth proceeds by two fundamental processes, surface diffusion and nucleation of adlayer clusters [1, 5]. Recently, a number of research groups have reported, that deposition of clusters rather than single atoms can lead to improvements of thin-film growth [6-8]. At present, the dynamics of even atomic deposition in the hyperthermal energy range (below 100 eV) are hardly understood, and for cluster-surface collisions there are scarcely data, where impact conditions and cluster size have been systematically varied. Clusters as an intermediate state between condensed and uncondensed matter become more and more the subject of intensive scientific exploration [9-12]. There are mainly two facts responsible for this observation, namely: i) advanced experimental techniques permit generation and handling of clusters in large quantities, and ii) modern computing techniques are available, that allow for the first time to theoretically treat clusters as a troublesome manybody problem [13]. From the view of crystallography the role of clusters in crystal growth, particularly in crystal growth from the vapour phase, becomes of increasing interest, because newly developed evaporation techniques, as e.g. laser pulse deposition, electron beam evaporation and sputtering result in an increased number of clusters as primary constituents of the deposition beams [14]. Finally there are experimental and theoretical hints for the existence of a so-called 'near-surface transition layer' (NSTL) in MBE, that support the idea of cluster involvement in MBE growth even in the case of monomers being the only constituent of MBE-beams [15]. Obviously the existence of such a transition layer results in a considerable raise of particle interactions just prior to their final input into the crystal; consequently the NSTL exhibits to some extend cluster properties.

2. CLUSTERS IN IONIZED CLUSTER BEAM TECHNIQUES

While a final proof for cluster involvement in traditional MBE is still to provide, cluster participation in laser pulse deposition and ICBD is obvious. In ICBD slightly ionized clusters of some hundred to some thousand atoms in size are accelerated towards the substrate by an electrostatic field, the voltage of which covers usually the range of 1 ... 10 kV. A kinetic energy of some tenth of an eV to some eV per atom is transferred to the substrate, with the result of enhanced surface migration. This in combination with the geometrical similarity of the surface structure and the atomic arrangement in the clusters leads to good single crystal quality even in the case of high growth rates and low substrate temperatures [14]. The cluster formation process is comparatively well understood now. On the other hand, little attention was paid to the microscopic picture of the processes that occur after a cluster has hit the surface of a growing film. The cluster formation process is comparatively well understood now. On the other hand, little attention was paid to the microscopic picture of the processes that occur after a cluster has hit the surface of a growing film.

Hardly more than correlation's of macroscopic parameters, like acceleration voltage with the quality of grown layers, are reported in literature [16]. In the case of clusters with strongly bound atoms the average binding energy per atom can amount to 1 ... 5 eV and therefore exceed the typical kinetic energy per atom in ICBD by a factor of 10. It seems not unlikely that the impinging clusters will not absolutely be atomized after having hit the surface, but will break down into smaller clusters, particularly into 'building blocks' and arrangements with 'magic numbers'. We suppose that the input of complete clusters of that kind is an elementary step in the ICBD-growth as well as in MBE under the participation of a near-surface transition layer.

3. DETECTIÓN OF CONDENSED CLUSTERS

If complete clusters or parts of them are incorporated into a growing layer (of course, under rearrangement of their atoms according to the single crystal substrate) the neighborhood-relations of the cluster would be frozen into the crystal. In other words: Let B be an atom next to atom A in the cluster, then B can be expected to be found in the neighborhood of A in the crystal. Consequently, if one marks the atomic arrangement in the clusters, the resulting pattern should be detectable in the grown crystal. The most promising method of 'marking' might be the use of isotopes, that do not influence physics and chemistry of growth. The task is then to investigate the isotope distribution in the grown crystal by appropriate isotope-sensitive analyzing tools. Clusters of comparatively high binding energy exhibit covalent bonds, as e.g. that of group-IV elements. Furthermore, in the case of silicon- or germanium homoepitaxy by ICBD, the clusters are naturally 'stoichiometric', which is usually not valid for clusters of alloys (GaAs-clusters are in general not of $(GaAs)_n$-kind). Hence the incorporation input of large clusters into the growing surface should be favored in the case of grupe IV element-epitaxy. We discuss here the following experiment: Two separate cluster sources provide beams of isotope-pure ^{28}Si- and ^{29}Si-clusters directed toward a silicon epilayer. Provided, the clusters become totally atomized after having hit the surface, the ^{29}Si isotopes will become homogeneously distributed in the ^{28}Si-matrix of the wafer surface. In the other extreme where the cluster do not disintegrate, domains of ^{29}Si can be expected (fig. 1). A distinction between these different modifications may be made by means of nuclear magnetic resonance (NMR). ^{29}Si has a net magnetic momentum (spin j = ½), while ^{28}Si (and ^{30}Si) does not. It is a well known fact, that protons and neutrons possess a spin. In particles the observable manifestation of spin may eliminate itself by pairing up spins having opposite sings. When placed in a magnetic field of strength B, a particle with a net spin can absorb electromagnetic radiation of energy $h\nu$. The frequency ν depends on the gyromagnetic ratio, γ of the special particle: $\nu = \gamma \cdot B$. Each spin aligns in one of the two possible orientations. The number of spins in the lower energy level, N^+ is usually higher than the number N^- in the upper level: $N^-/N^+ \sim e^{-E/kT}$. Here E is the energy difference between the two spin states, k is Boltzmann's constant and T is the absolute temperature [18].

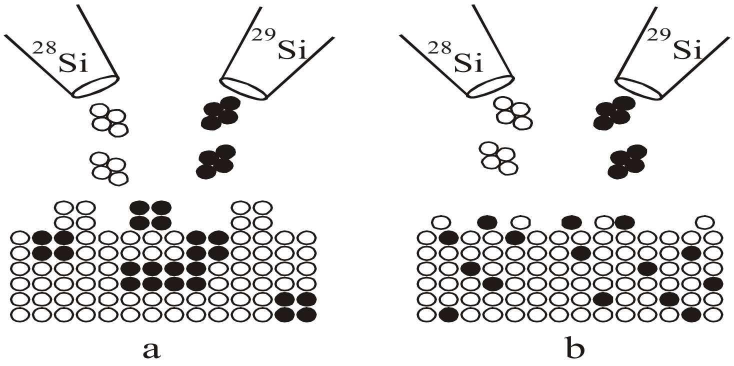

Fig. 1: Schematic representation of an experimental setup for the marking of isotopes during epitaxial growth, where (1) and (2) are cluster sources for clusters of isotope 1 (as e.g. ^{28}Si) or of isotope 2 (as e.g. ^{29}Si), respectively. a) clusters become incorporated as a whole (in the extreme case). b) clusters become fully atomized after having hit the surface.

Let the mole fraction of ^{29}Si be comparatively small, but (because of signal intensity) not too small: say about 5 %. Then in the case of a homogeneous distribution, a ^{29}Si-atom will normally be surrounded by ^{28}Si-atoms, which means: it is placed in an unmagnetic region. Completely different is the situation in case of domains: Now, the average neighbor of a^{29}Si-atom will be one of the same kind, the neighborhood is a magnetic one. The interaction of the nuclear magnetic momentum with the magnetic fields, arising from the neighboring atoms, will give rise to spin-spin coupling and energy level splitting, and should thus be detectable by NMR.

4. OUTLINE OF THE EXPERIMENTAL APPROACH

In NMR, the experiment monitors the reversal of nuclear magnetic moments. Every nucleus with spin, as in the case of ^{29}Si, pocesses a magnetic moment, and the energy of a nucleus of spin quantum number I with projection m_I, in a magnetic field B is

$$E_{\mathrm{mI}} = -\mathrm{g_I} \cdot \mu_\mathrm{N} \cdot \mathrm{m_I} \cdot B \qquad (1)$$

where $\mathrm{g_I}$ is the nuclear g-factor, and μ_N is the nuclear magneton, $e\hbar/2m_p$.

Protons display a value of $g_I = 2.79270$ (hydrogen), and their NMR frequency at an external magnetic field of 1 T falls into the radio-frequency range of 42.577 MHz:

$$h\nu = ½\, g_I\, \mu_N\, B - [-½\, g_I\, \mu_N\, B] = g_I\, \mu_N\, B \qquad (2)$$

corresponding to a resonance transition of the proton from its lower (+) to its upper (-) spin state. The population difference at a field B and temperature T is given as

$$(N^{+}-N^{-}) / (N^{+}+N^{-}) \sim \tfrac{1}{2}\, g_I\, \mu_N\, m_I\, B / kT, \qquad (3)$$

which for 1.5 T at room temperature gives a value as low as $2.6 \,.\, 10^{-6}$. The excess of lower spin population over the higher spin population is thus very small. At higher magnetic fields is the signal intensity correspondingly greater, as the population difference is increased.The resonant magnetic moment of the nuclei interacts with the so-called local field, which differs from the externally applied field because of the currents, the latter might stir up in the electrons of the cluster. Let us express the local field as

$$B_{loc} = (1 - \sigma)\, B \qquad \text{where } \sigma \text{ is called the shielding constant.} \qquad (4)$$

The protons experience an extra contribution of $-\sigma B$ to the overall field, and if situated in different chemical environments, have different shielding constants with the resonance condition satisfied at different values of B. The extra field σB is called the chemical shift of the group of protons. A fine structure of the spectrum, i.e. the splitting of groups into individual lines occurs as a consequence of the magnetic interactions between the nuclei in the ^{29}Si cluster. No such interactions would exist in an ^{28}Si environment. The direct dipole-dipole interactions makes an important contribution to the spectra of solid samples. At a ^{29}Si crystal site a distance R from a proton with spin projection m_I there is a magnetic field given by

$$B_{nucl} = g_I\, \mu_N (\mu_o / 4\pi)(1/R^3)(1-3\cos^2\theta) m_I. \qquad (5)$$

The quantities R and θ are defined in figure 2. Applying crystal site distances of 3 Å, this field is of the (quite small) order of 100 μT. It becomes now clear, that isolated ^{29}Si atoms in an environment of unmagnetic ^{28}Si display a single unsplit line. Neighbouring ^{29}Si atoms in a two-atom cluster would first split into two by virtue of the two orientations of one of the ^{29}Si protons, and then each line is split again as a result of the interaction with the second proton. Three equivalent ^{29}Si protons in the cluster give rise to four lines in the intensity ratio 1:3:3:1. In general, N equivalent protons in a ^{29}Si cluster split a neighboring group into (N+1) lines in the intensity distribution of Pascals triangle:

N	intensity distribution
0	1
1	1 1
2	1 2 1
3	1 3 3 1
4	1 4 6 4 1

Consequently, such resonance is split into three lines with an intensity ratio 1:2:1.

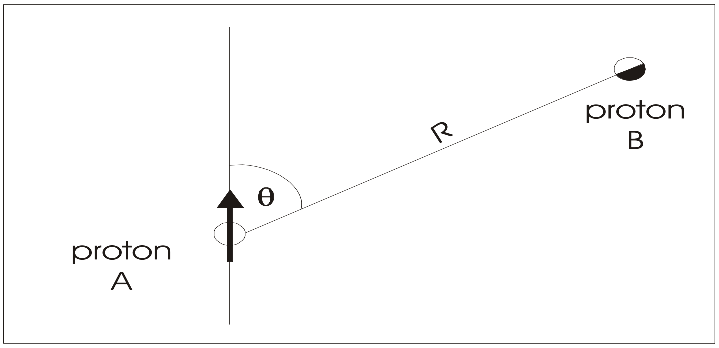

Fig. 2 Angle θ and distance R involved in the dipole-dipole interaction

Of course might a superposition of spectra groups occur if the chemical shift is small and comparable to the effect of spin-spin interaction. As the latter is independent from the external field, but the former is proportional to B as σB, an increased field might be helpful in resolving groups of lines, leaving the fine structure unchanged.

5. OTHER ANALYZING TOOLS

Apart from magnetic properties, isotopes of a special element are primarily different in their mass. The latter influences oscillation frequencies, that are inversely proportional to the square root of the oscillator mass. Infrared and Raman-spectroscopy as well as high resolution electron energy loss spectroscopy (HREELS) present further methods to investigate the isotope distribution. However, one would try to use isotopes with mass differences as large as possible. In the case of silicon the isotopes ^{28}Si and ^{30}Si can be used with a mass difference of 2 a.m.u., corresponding to 7%. Germanium as the next representative of group-IV elements is expected to behave similar to silicon with respect to the growth mechanism. By using the lightest (^{70}Ge) and heaviest stable isotope (^{76}Ge), we get a mass difference of 6 a.m.u., or 8%. For NMR, however, Ge is not a useful element, since the only active nuclide, ^{73}Ge, has a spin of $j = 9/2$, that gives rise to multiplett splitting with overlaps, and translates into broad signal lines.

CONCLUSIONS

Ultrathin layer systems like multi-quantum wells and superlattices are of considerable interest for both basic research and microelectronic applications. These systems however are thermodynamically metastable, and much care must be taken in a successful preparation. Kinetically controlled methods, like MBE, are predestinated to that end. A full exploitation of their capabilities requires insight into the microscopic picture of growth, which might be influenced by the presence of clusters.

The signal in NMR spectroscopy results from the difference between the energy absorbed by the spins which make a transition from the lower energy state to the higher energy state, and the energy emitted by the spins which simultaneously make a transition from the higher energy state to the lower energy state. The signal is thus proportional to the population difference between the states. NMR is a rather sensitive spectroscopy since it is capable of detecting these very small population differences. It is the resonance, or exchange of energy at a specific frequency between the spins and the spectrometer, which gives NMR its sensitivity [19].

The question whether Si-clusters are pinned to the growing epitaxial Si-film and flattened on impact, or the footprint of the clusters on the surface is significantly reduced, can be answered by isotope marking and the application of isotope-sensitive analytical methods, as shown in the present paper.

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