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FORMATION OF CLUSTER IONS OF PHOSPHORUS ATOMS IN PULSED-LASER STIMULATED FIELD EVAPORATION OF GALLIUM PHOSPHIDE

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Cluster ions of phosphorus atoms, P_2^+, P_3^+, P_3^{2+}, and P_4^+, are formed in pulsed-laser stimulated field evaporation of gallium phosphide. The ion distribution varies with field strength and laser power density and can be clearly divided into three regimes. We clearly certified this kind of variation of appearance of field evaporated ions for the first time in semiconductors. This phenomenon also implies that the pulsed-laser with sufficient power induces not only the field evaporation but also the agglomeration of phosphorus atoms. Accordingly, pulsed-laser stimulated field evaporation of gallium phosphide is not merely a thermal activation process.

1. Introduction

Although the atom probe method is known as one of the most sensitive techniques available in microanalysis and gives us more detailed information on microstructures such as silicon oxide and silicon–silicon oxide interfaces [1], or semiconductors and their metal surfaces [2,3] which information is indispensable for progress in electronics, the process of field evaporation playing a very important role in the method is not well understood and needs further study.

At first an atom probe field ion microscope (AP-FIM) using high voltage pulses was used and recently a pulsed-laser AP-FIM has been used. When studying field evaporation of silicon in ultra high vacuum, formation of cluster ions is of a great interest. Studying the anomalous field evaporation of silicon using high voltage pulses, Sakurai et al. [4] concluded that cluster field formation resulted from microscale rupture due to Maxwell stress from the high electric field. If their idea can be applied to the pulsed-laser stimulated field evaporation mechanism, cluster formation is not expected to occur when a semiconductor tip is at a high temperature because of the smaller field penetration depth. But using laser pulses, Kellogg found [5] that at temperatures above 1000 K, cluster ions of silicon field evaporated and reported [6]

that the anomalous field evaporation (random cluster formation) observed at low temperature was replaced by a uniform and layer-by-layer field evaporation at temperatures above 150 K and that pulsed-laser stimulated field evaporation of silicon might be a thermally stimulated process. On the other hand, Tsong [7,8] also found that the abundance of the cluster ions increases with laser intensity and the species of cluster ion was related to the highly symmetric, small units of atoms existing in silicon. He also pointed out that photoexcitation played an important role in pulsed-laser field evaporation of silicon and that pulsed-laser field evaporation could be sustained almost indefinitely by a field-gradient- and temperature-pulse-induced surface diffusion of silicon atoms from the emitter shank.

Thus, when high voltage pulses were replaced by laser pulses, considerable differences were found. These findings tempted us to investigate the field evaporation of compound semiconductors in ultra high vacuum using a pulsed-laser atom probe. In this paper, we report that different regimes of pulsed-laser stimulated field evaporation of gallium phosphide are clearly established depending on the applied field strength and laser power density, which gives suggestions about the effect of the laser pulse in the field evaporation process.

2. Experimental method

A schematic diagram of the pulsed-laser atom-probe field ion microscope (PLAP-FIM) used in this experiment is shown in fig. 1. Most parts of this system are the same as used in the combined-type time-of-flight (TOF) atom-probe field ion microscope (AP-FIM) of Murakami et al. [9]. Accordingly, the used PLAP-FIM is able to detect neutral particles formed in the field evaporation process. In this experiment, only a conventional linear-type mass spectrometer with a 189 cm flight path was used. Ions are detected with a 6 mm chevron channel plate. The flight time of the ions is measured by an 8-channel electric digital timer whose resolution is 5 ns. The 10 ns laser pulse from a Molectron UV-22 nitrogen laser (main wave length = 337 nm) is directed by a mirror and focused on the tip. The light intensity can be gradually changed by sliding the optical lens. Although the average power density of the laser pulse is about 5×10^6 J/cm^2 before reaching the mirror according to the specification, the resulting light intensity is not so exact because of an unequal distribution of the intensity on the microscopic area of the surface of the tip. The repetition rate of laser pulse was fixed to 10 per second.

The atom probe sample was prepared in the same way as done by Ohno et al. [10]. A GaP whisker grown by the vapor–liquid–solid (VLS) mechanism was chemically etched in a solution of HNO_3 : HCl = 1 : 3 at about 330 K until

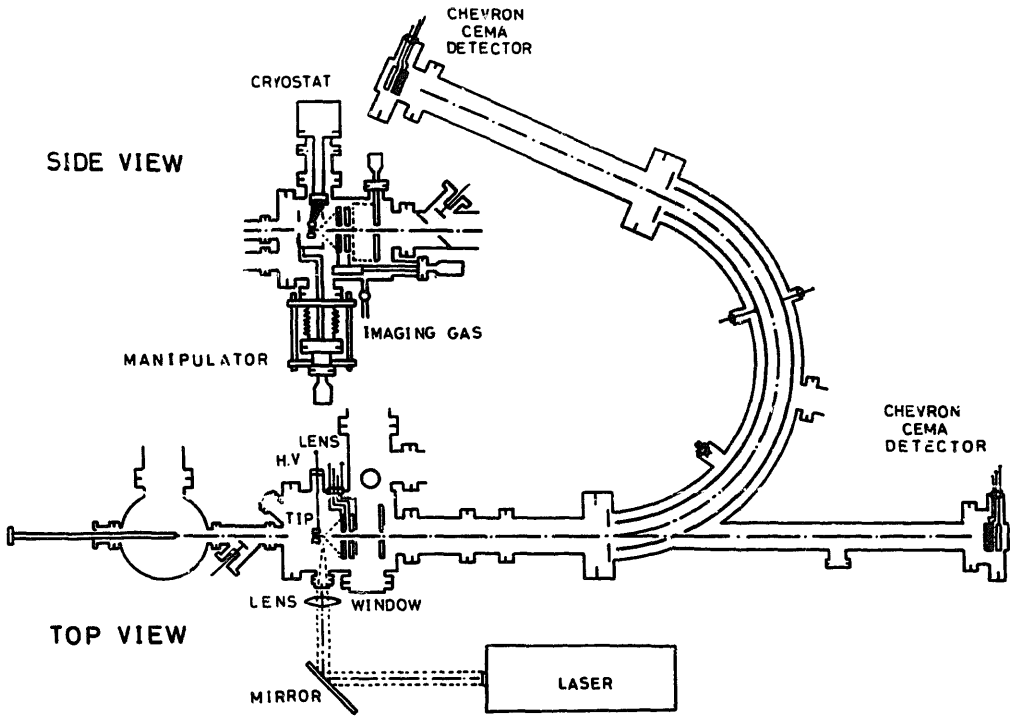

Fig. 1. Schematic diagram of the pulsed-laser TOF atom probe field ion microscope.

a needle shaped specimen with a tip radius of a few hundred ångström was obtained. The other end of the tip was inserted into a Pt tube held at a positive bias voltage. The tip can be cooled down to about 50 K by a cryogenic refrigerator.

With the aid of a mini computer NOVA 4/C, for each laser pulse, the TOF data are stored together with the DC voltages and the total ion count between pulses and the reduced TOF spectrum is plotted automatically. All data presented here was obtained in a vacuum of about 3×10^{-9} Torr. No gas was introduced.

3. Results and discussion

Although Celezo et al. [11] reported that a pulsed-laser atom probe FIM had been used to obtain a stoichiometrically correct analysis of GaAs and InAs, such an analysis could not easily be done in our experiment. In spite of this nuisance, the following characteristic phenomena were found in our measurement system.

No neutral atom was detected. The observed mass spectrum gave Ga^+, P^+, P_2^+, P_3^+, P_4^+, P^{2+}, and P_3^{2+}. The stable isotopes of gallium were well separated.

Gallium ions of the form Ga^+ and phosphorus cluster ions of the form P_3^+ were the most common species identified.

It is not possible that the spectrum of Ga^+ conceals that of Ga_2^{2+} because these two stable isotopes of gallium (mass = 69, 71) are well separated and half integral m/n lines should have appeared as pointed out by Tsong [7,8]. This kind of identification of ion species, however, cannot be applied to the phosphorus ions because phosphorus isotopes are absent. To avoid this problem, we measured the amount of each field-evaporated atom. Generally, an increase of the amount of phosphorus atoms by considering singly charged ions as double charged ions is unavoidable and effects the P/Ga ratio. For example, if the identification of the ion species in fig. 2a is correct, the total amount of gallium and phosphorus atoms is respectively 1347, 1427 giving a P/Ga ratio of 1.06, where the numbers of P^{2+}, P^+, P_3^{2+}, P_2^+, P_3^+, and P_4^+ are 14, 98, 58, 263, 189, and 12, respectively. However, if the spectrum of P_2^+ were P_4^{2+}, the total amount of gallium and phosphorus atoms is respectively 1347, 1953 giving a P/Ga ratio of 1.45. This result is not within the expected statistical fluctuation of the data and shows that this assumption is unreasonable. The identification of the other phosphorus ionic species is based on the same idea and notable regularity becomes apparent.

As shown in figs. 2a–2c, different regimes of pulsed-laser stimulated field evaporation of gallium phosphide were found depending on the applied field strength and laser power density as certified in metals [12], and clearly certified for the first time in semiconductors. As shown in fig. 2a, in the first regime near the onset of field evaporation and for a laser power density of 3×10^6 J/cm^2, P^+ and P_2^+ are formed in addition to Ga^+ and P_3^+. Doubly charged ions, P^{2+} and P_3^{2+}, were relatively abundant and cluster ion P_4^+ was rare. As shown in fig. 2b, in the second regime of low electric field and high laser power density, the singly charged ions P^+ and doubly charged ions, P^{2+} and P_3^{2+}, which were seen in the first regime almost disappeared. Accordingly, most of the phosphorus ions were cluster ions. As shown in fig. 2c, in the third regime of lower electric field and higher laser power density, the distribution of the cluster ions of phosphorus atoms changed. The number of cluster ions of P_4^+ exceeded that of P_2^+. This considerable trend was also seen for $(\bar{1}00)$, (110), (111), and $(\bar{1}\bar{1}\bar{1})$ crystalographic planes with the tip temperature before irradiation by the pulsed-laser at about 50 K or room temperature.

More than two phosphorus atoms cannot gather together to form a cluster unless they feel the existence of the nearest phosphorus atoms and have enough energy to come across. Accordingly, these results suggest that a laser pulse with sufficient energy can disturb the structure of the surface atoms, especially the phosphorus atoms, in the gallium phosphide system in a high electric field, though gallium phosphide is a covalent bonding rigid crystal. According to our calculation [13], the maximum surface temperature giving the results of fig. 2b and 2c is about 600 and 900 K, respectively. Therefore,

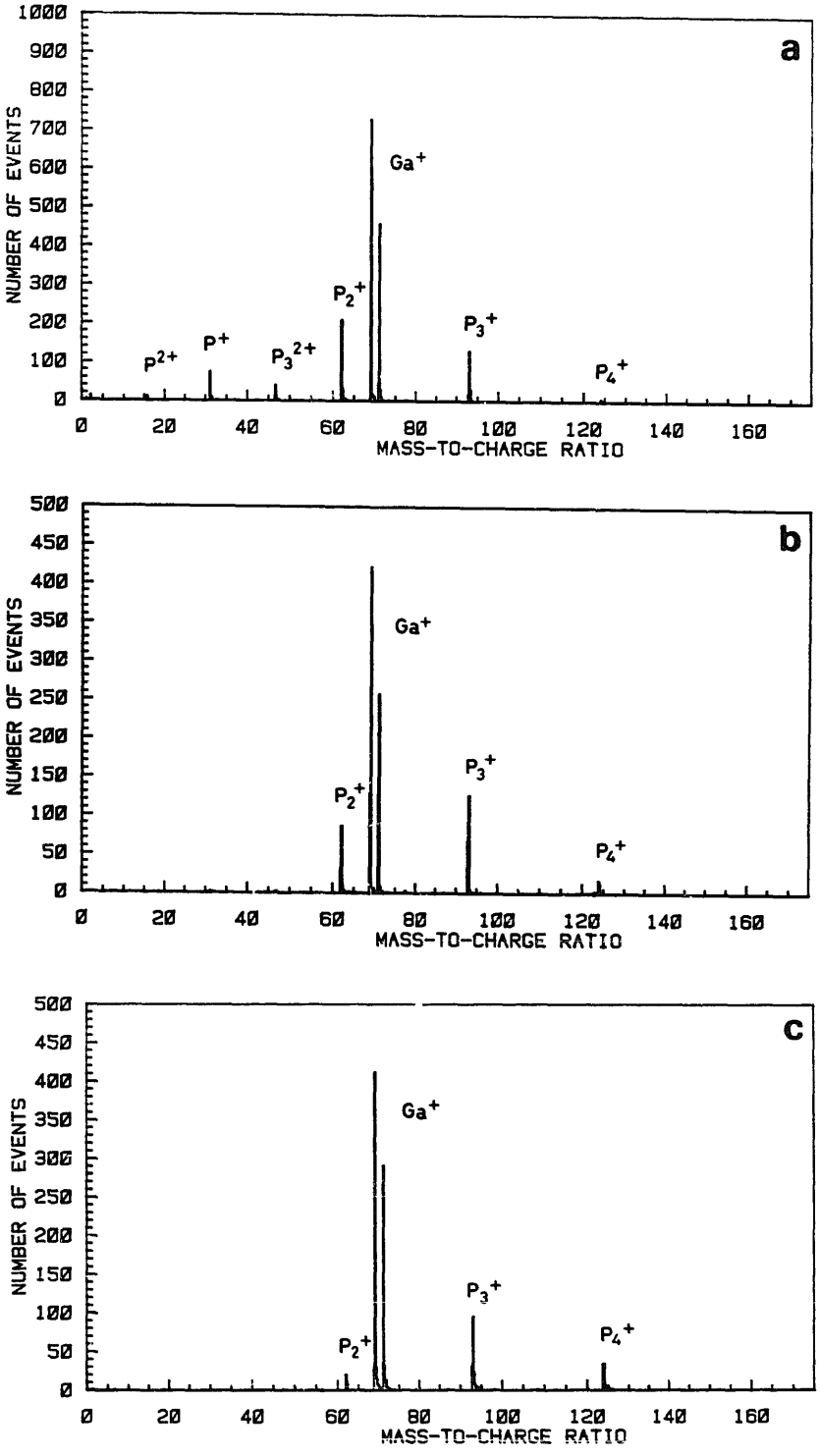

Fig. 2. Atom-probe mass histograms of gallium phosphide on the ($\bar{1}00$) plane at about 50 K. (a) Applied voltage: 10.6 kV, laser power density: 3×10^6 J/cm^2, P/Ga: 1.06. (b) Applied voltage : 8.4 kV, laser power density: 5×10^5 J/cm^2, P/Ga: 1.09. (c) Applied voltage: 6.1 kV, laser power density: 1×10^7 J/cm^2, P/Ga: 1.07.

cluster formation of phosphorus atoms, P_2 and P_4, seems to need an energy corresponding to a temperature of at least 500 K for the gallium phosphide system in a high electric field.

In addition, comparison with the formation energy of cluster ions in the case of no electric field seems to lead us to a better understanding of how laser-stimulated field evaporation occurs. In case of no electric field, the formation energy of P_4 is less than that of P_2 which is less than that of P [14]. Accordingly, in the gallium phosphide system, the interaction between phosphorus atoms can induce agglomeration of phosphorus atoms and cluster formation. If the effect of the high electric field is neglected, the expected distribution of cluster ions of phosphorus atoms will differ significantly from the results obtained. It can be considered that in the first regime corresponding to fig. 2a, a single phosphorus atom in the top surface layer gains enough energy only to escape from the surface, but not to interact with other phosphorus atoms when irradiated by the pulsed-laser because of insufficient energy of the pulsed-laser. On the contrary, it can be considered that in the second and third regimes, a single phosphorus atom in the top surface layer gains enough energy not only to escape from the surface but also to interact with other phosphorus atoms when irradiated by the pulsed-laser because of sufficient energy of the pulsed-laser. In spite of the lower formation energy necessary to form P_4 clusters in the case of no electric field, the obtained results seems to show that the pulsed-laser energy necessary to form P_4^+ cluster ions is higher than that to form P_2^+ cluster ions.

Meanwhile, the existence of the phosphorus cluster ion P_3^+ adds more difficulties to the explanation of the process of pulsed-laser stimulated field evaporation of gallium phosphide. The low energy tail of the Ga^+ mass line is one of the complexities of pulsed-laser stimulated field evaporation. It can also be considered that the high electric field of the order of several volts per ångström mainly causes the reduction of the activation energy of the appearing ions in stead of variation of the distribution of phosphorus cluster ions.

Anyhow, it is to be regretted that we are unable to discuss the experimental results further because of the lack of basic parameters such as the ionization potential of P_2 and P_4. However, it is clearly certified that the ion distribution varies with field strength and laser power density and can be clearly divide into three regimes. It can also be concluded that pulsed-laser stimulated field evaporation of gallium phosphide is not merely a thermal activation process.

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