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Neutral and Ionic Particle Emission from a GaAs Surface Induced by the (harmonic) Frequencies of the Nd:YAG Laser

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The emission of ionic and neutral particles, resulting from irradiation of a GaAs surface by 1064, 532, 355 and 266 nm *Q*-switched Nd:YAG laser light, has been studied. Incident laser power densities up to 9.6×10^7 Watts/cm^2 have been applied. For 1064, 532 and 355 nm radiations the ratios of ionic to neutral particle emissions are close to the thermal ratio corresponding to the boiling point of Ga. In the case of 266 nm radiation this ratio appears to be higher, which is probably due to non-thermal ion contributions. For several incident wavelengths the emitted yields of ions and neutrals varied with the fifth power of the incident laser power density. The wave form of the emitted ion pulse and the recorded mass spectrum after irradiation at 266 nm differ significantly from those obtained at the other applied wavelengths.

KEY WORDS: Particle emission from GaAs surfaces; Laser irradiation of surfaces.

1. INTRODUCTION

Recently, some experimental studies have been performed concerning the particle emission from a GaAs surface as a consequence of irradiation by (unfocussed) Nd:YAG and ruby laser beams.[1,2] Such studies yield data which can be used to estimate the substrate losses if laser irradiation is applied for the annealing of ion-implanted semiconductors.

It appeared that laser irradiation of GaAs by 1064 nm Q-switched Nd:YAG laser light resulted in the emission of mainly Ga^+ atomic ions, Ga atomic neutral and As_2 neutral molecules.[1] The experimentally determined ion-neutral ratio was found to be close to the calculated one, corresponding to the boiling point of Ga (2676 K), using the Langmuir–Saha equation.[1] In experiments with ruby laser light incident on GaAs, the application of Rutherford-Back-Scattering revealed that gallium and arsenic were emitted in equal amounts[2]; this result differs from the assumption made in Ref. 3 that only arsenic contributes to the evaporating species.

In the present work the ion and neutral emissions of particles from GaAs have been studied at both the fundamental and the second, third and fourth harmonic frequencies of a Q-switched Nd:YAG laser; the corresponding wavelengths are 1064, 532, 355 and 266 nm, respectively. Further, the ion emission has been measured as a function of the incident power density at several wavelengths, using an electrical diode set-up. By weighting the cathode of the diode the total emitted mass has been determined. The measurement of the temporal wave form of the emitted ion pulses yields information about the kinetic energy of the released particles and of the time character of the emission process.

2. EXPERIMENTAL

The apparatus used in the present experiment is essentially the same as that applied in Ref. 1, and will therefore only briefly be described here. Basically, it consists of a (1–200 a.m.u.) quadrupole mass spectrometer (QMS) placed inside a vacuum chamber which is equipped with a sapphire window for the transmission of the laser light. The GaAs target is placed inside the ionization chamber of the QMS, such that it can be hit by the laser beam. The ionizing electron beam (i.e.b.) of the QMS can be switched off or on, permitting the observation of directly laser-ionized particles or of neutral particles, respectively. The QMS signals are fed into the 50Ω input channel of a gated integrator, the gate (width 50 ns) being synchronized to the laser pulse. By scanning the mass range of the QMS (1 a.m.u. per 15 laser pulses) and averaging the obtained signals, a mass spectrum is recorded. The entire mass spectrum is the result of about 3000 laser pulses and is obtained in 300 seconds.

For measuring the ion-neutral ratio an electrical diode set-up is applied. The anode (target) is set at +500 V and the (collecting) cathode is connected with the 50 Ω input of the gated integrator. By scanning the time delay between the laser pulse and the detection gate, the wave form of the emitted ions can be registered; integration of the wave form with respect to time yields the emitted charge per laser pulse. The total of the emitted particles (ions + neutrals) is determined by weighting the cathode before and after the experiment.

The incident radiation is provided by a Q-switched Nd:YAG laser. The laser delivers 10 ns long pulses at a repetition frequency of 10 Hz containing up to 0.7 Joules per pulse at 1064 nm. Harmonics generation via non-linear optical crystals yields the outputs at the other wavelengths (532, 355, 266 nm, respectively). The application of lenses makes it possible to decrease the effective diameter of the laser beam and thus to vary the power density.

The cross-sectional spatial distribution of the intensity in the laser beam varied ±5, ±10, ±15 and ±25% for the 1064, 532, 353 and 266 nm radiations, respectively. Taking into account the temporal behaviour of the (harmonic frequencies) laser pulses, the relation between the energy density E and the power density P has been set equal to: $P = E/10^{-8}$ Watts/cm^2.

3. RESULTS

3.1. Mass spectra

The mass spectra obtained for incident radiations at 1064, 532 and 355 nm, in the range $5\text{-}7 \times 10^7$ Watts/cm^2, are similar in appearance. As an example, the spectrum corresponding to 1064 nm radiation is shown in Figure 1a. The main feature in the obtained "$h\nu$ spectra" (no i.e.b. present) is the presence of Ga^+ atomic ions at $m/e = 69$ and 71; in addition, a small amount ($\ll 1\%$) of Ga_2^+ molecular ions is present at $m/e = 138$, 140 and 142 (not shown in Figure 1a). By switching on the i.e.b., the "$h\nu + el$ spectra" are obtained, revealing the presence of neutral As_2 at $m/e = 150$ (and of neutral Ga atoms) in the evaporated species. Besides, a small contribution ($\ll 1\%$) of neutral molecular GaAs at $m/e = 144$ and 146 is observed. The atomic arsenic peak at $m/e = 75$ is mainly due to dissociative ionization of As_2 by the i.e.b., as has been explained in Ref. 1. The dominant

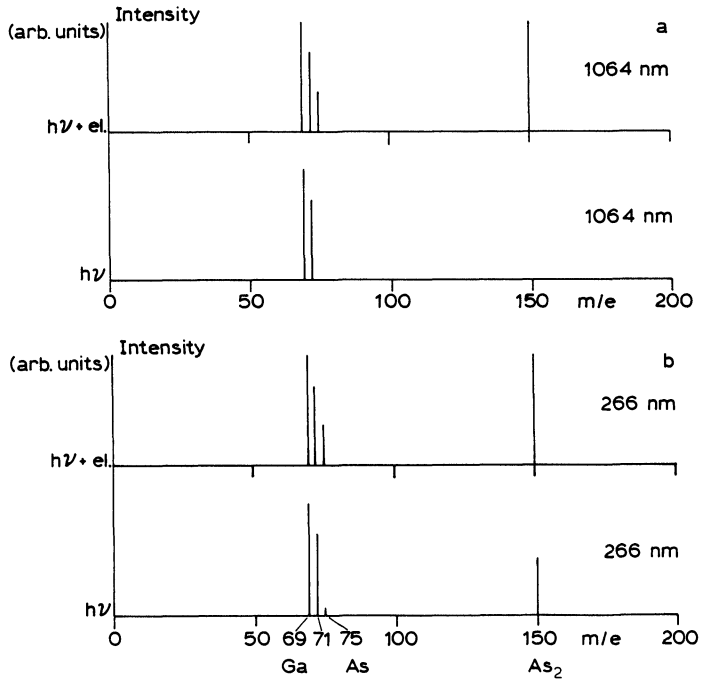

FIGURE 1 Mass spectra obtained for incident power densities in the range $5\text{–}7 \times 10^7$ Watts/cm^2. (a) for 1064 nm radiation, (b) for 266 nm radiation on GaAs.

appearance of atomic Ga and molecular As_2 is in accordance with the thermodynamics at high temperature (2676 K).[4]

The mass spectrum obtained at 266 nm incident radiation, however, shows differences in comparison to those obtained at the other applied wavelengths. For at 266 nm a significant contribution of directly laser ionized As_2^+ in the "$h\nu$ spectrum" (i.e.b. off) was observed, as can be seen in Figure 1b.

3.2. Power density dependence of the emitted particles

In Figure 2 the (pulse-averaged) QMS signals at $m/e = 69$ corresponding to directly laser ionized Ga^+ species (no i.e.b. present) are given as a function of the incident power density (P) in the range $1.2\text{–}7.4 \times 10^7$

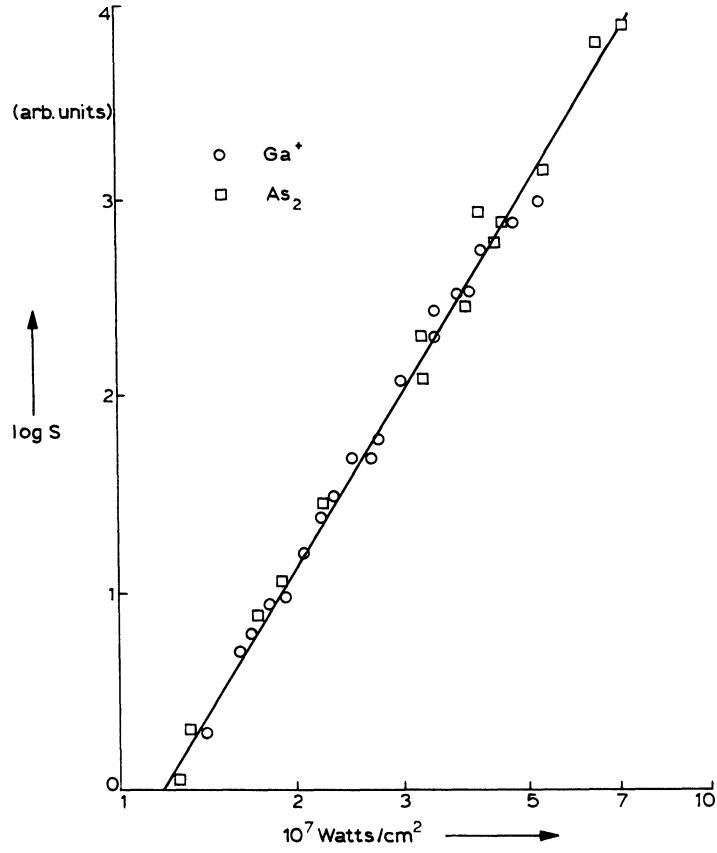

FIGURE 2 Power density dependence of emitted Ga^+ and As_2 particles for 1064 nm incident radiation on GaAs in the range $1.2\text{–}7.4 \times 10^7$ Watts/cm^2.

Watts/cm^2 for 1064 nm radiation. It appeared that the signal varies with the fifth power of P. For higher power densities the slope tends to level off. Similar results as shown in Fig. 2 have been obtained for the other wavelengths applied.

The formation of neutral As_2 molecules, which has been detected via ionization by the i.e.b., shows the same dependence on P at 1064 nm as found for directly ionized gallium. The Ga^+ and As_2 plots, as presented in Fig. 2, have been normalized relative to each other.

3.3. Ion-neutral ratio of emitted particles

In the case of 1064, 532 and 355 nm radiations, the experimentally obtained ion-neutral ratios in the power density range $5\text{-}13 \times 10^7$ Watts/cm^2 are given in Table I. It can be seen that they all exhibit about the same value, and lie in the range $3.6\text{-}4.5 \times 10^{-4}$. These values are close to the calculated ratio using the Langmuir-Saha equation at the temperature of 2676 K, which is the boiling point of gallium. However, at 266 nm the experimentally derived ratio is significantly higher than those corresponding to the other wavelengths.

3.4. Total emitted mass vs. incident power density

In Figure 3 the total emitted mass is depicted as a function of the incident laser energy density (Joules/cm^2) for several applied wavelengths. Energy densities are chosen here, instead of power densities, to permit a comparison with data obtained by other groups.

In the present work the total emitted masses have been obtained by weighting the cathode of the electrical diode before and after the experiment. The plot in Figure 3 suggests that the emitted mass depends on the fifth power of the incident energy density in the range below 0.7 Joules/cm^2; for higher energy densities the slope of the curve appears to level off. These features are about the same as found for the particle emissions described in Section 3.2.

Although the ion-neutral ratio obtained at 266 nm radiation differs from that of the other wavelengths, the total emitted mass appears to join that of the other incident radiations.

TABLE I

Experimental and calculated ion-neutral ratios (n^+/n_0) at several incident radiation wavelengths

λ (nm)	Joules/cm^2	10^7 Watts/cm^2	n^+/n_0
1064	0.5-1.35	5-13.5	3.9×10^{-4}
532	0.58	5.8	3.6×10^{-4}
355	0.65	6.5	4.5×10^{-4}
266	0.75	7.5	1.2×10^{-3}
thermal[a]	—	—	3.8×10^{-4}

[a] Corresponding to the boiling point of Ga (2676 K) and applying the Langmuir-Saha equation.

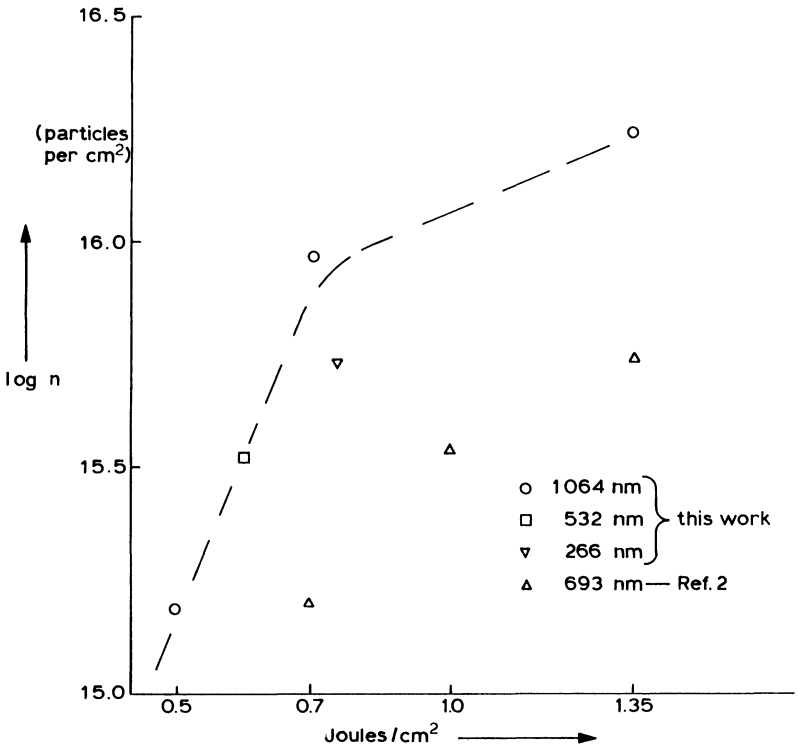

FIGURE 3 Energy density dependence of the total emitted mass at several incident wavelengths in the range 0.5–1.35 Joules/cm^2. Data points corresponding to ruby laser irradiation of Ref 2 are also included.

The mass losses owing to irradiation at the ruby laser wavelength and calculated from the corresponding Rutherford-Back-Scattering experiments of Ref. 2 have also been presented in Figure 3 for some energy densities. The calculated losses in the case of ruby laser irradiation are about three times lower than the losses found in the present Nd:YAG laser experiment by weighting the cathode. The energy density dependence seems to follow the same behaviour in either case.

3.5. Ion pulse waveform

In Figure 3 the temporal character of the emitted ion pulses is shown for the incident wavelengths 1064, 532 and 266 nm and for 7×10^7

Watts/cm^2 power density. These curves have been derived by scanning the delay of the detection gate for the signals coming from the cathode, with respect to the laser pulse.

Some differences between the depicted wave forms are clearly visible. At 1064 nm the initial peak is followed by a long tail, the intensity of which is less pronounced for 532 nm radiation and practically absent in the case of 266 nm laser light.

Table II shows some characteristic data that have been derived by analysing the wave forms. It is seen that the pulse width corresponding to 266 nm radiations is about three times smaller than those at the other wavelengths. Moreover, the time of arrival of the main peak maximum for 266 nm is considerably shorter than for 1064 nm and 532 nm light.

4. DISCUSSION

It can be deduced from the experimental results that the particle emission characteristics of laser irradiated GaAs are about the same for 1064, 532 and 355 nm radiations. In the case of 266 nm light relatively more ions are emitted from the surface, as can be seen from the mass spectrum of Figure 1b and from the ion-neutral ratio in Table I. Efforts will now be made to explain this difference.

Calculations show that irradiating GaAs with a 20 ns long ruby laser pulse (693 nm), exhibiting an energy density of 1 Joule/cm^2 ($\simeq 5 \times 10^7$ Watts/cm^2), is sufficient to reach the boiling point of gallium at

TABLE II
Experimental values of some characteristic wave form parameters at several incident wavelengths

λ (nm)	*fwhm* (ns)[a]	t_{max} (ns)[b]	t_s[c]
1064	560	1200	850
532	650	1350	820
266	200	900	680

[a] Width of main peak at 0.5 of the maximum height.
[b] Arrival time of the main peak maximum.
[c] Time of the to zero intensity extrapolated leading pulse edge.

2676 K.[5] Applying the Langmuir–Saha equation[6] the ion-neutral ratio at this boiling point can be calculated to be 3.8×10^{-4}.[1] Now, the following conclusions are drawn, using the calculated ratio at 2676 K and the ratios experimentally obtained for 1064 nm light in the energy density range 0.5–1.35 Joules/cm^2:

—for 0.5 Joules/cm^2 (5×10^7 Watts/cm^2) Q-switched Nd:YAG laser light at 1064 nm the GaAs surface already reaches 2676 K, because the experimental and calculated ion-neutral ratios are about equal. Apparently, the (time dependent) effective absorptions at 693 and 1064 nm have similar characteristics.[7]

—increasing the energy density at 1064 nm does not lead to a higher surface temperature than the boiling point, because the ratio remains about the same; however, higher energy densities do lead to more emitted material.

—the heating and evaporation mechanisms at 532 and 355 nm are about the same at those at 1064 nm because there is practically no difference between the measured ion-neutral ratios at the three wavelengths. For each wavelength the boiling point is apparently reached for the applied energy densities; the higher absorption coefficients at 532 and 355 nm do not lead to temperatures higher than the boiling point.

—it is assumed that the surface temperature of GaAs does not exceed 2676 K in the case of irradiation at 266 nm because from the foregoing it seems that this temperature does not depend on the energy density (0.5 Joules/cm^2) or on the wavelength.

If the higher ion-neutral ratio found at 266 nm radiation cannot be due to a significantly higher surface temperature, another mechanism must be responsible for the observed difference. From the mass spectrum of Figure 1b it can be seen that directly ionized As_2 appeared. The ionization potential of As_2 is, however, relatively high (~9–9.5 eV) as can be derived from the spectral absorption features of As_2.[8] Therefore, the (calculated) thermal contribution to the ion formation of As_2^+ can be neglected (thermally ionized fraction $<10^{-10}$). It is suggested that photoionization of As_2 molecules by the incident 266 nm laser light takes place. A possible mechanism is that near-resonant two photon ionization of vibrationally hot As_2 ($X\ ^1\Sigma_g^+$), via the intermediate excited states A and B ($X\ ^1\Sigma_u^+$), results in the formation of the observed ions at $m/e = 150$. In addition the possibility remains that also Ga-atoms are subject to near-resonant two photon ionization.

The interpretation of the shape of the obtained wave forms in Figure 1 is rather difficult. It is clear that there are differences between the temporal ion emissions for different incident wavelengths (see Table II and Figure 4). For the longer wavelengths the main peak maximum is located at longer times and joined by an emission tail. It is known that space charge effects may influence the time width and the speed of the ion cloud, whereas displacement currents in the diode may affect the detected pulse shape.[9] Nevertheless, it seems that several microseconds after the ions laser pulse ions are still detected and thus emitted from the GaAs surface, especially in the case of 1064 nm radiation.

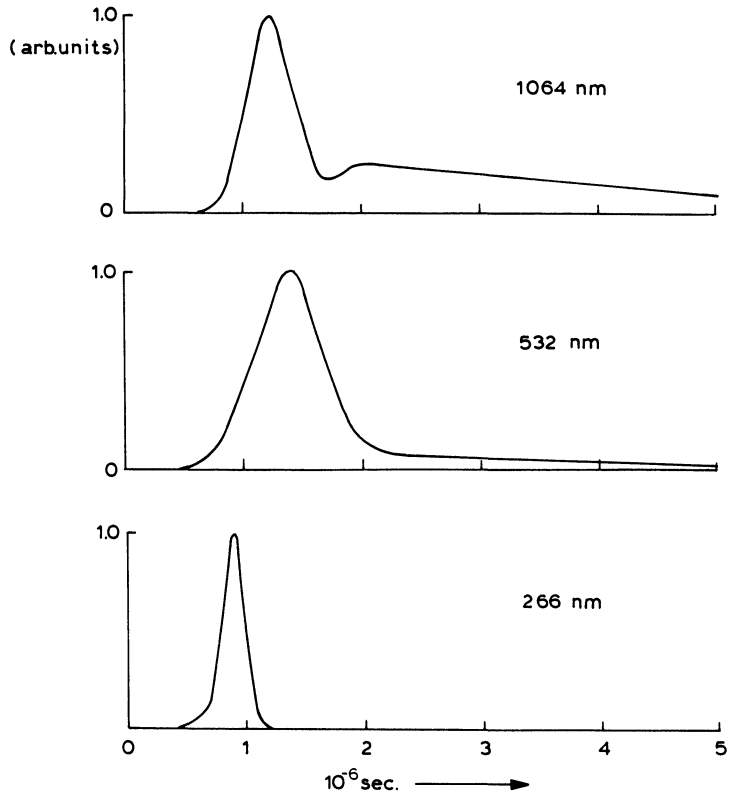

FIGURE 4 Ion pulse wave forms obtained for several incident radiation wavelengths on GaAs.

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