

The $\text{Al}_x\text{Ga}_{1-x}\text{As}$ interface with GaAs is known to be a very close lattice match and to have low interface recombination. Unfortunately it has been reported² that the conduction band contains an electron affinity barrier, typically approaching 0.5 eV for a high aluminum content of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$. A comparable barrier may be expected between Ge and $\text{Al}_x\text{Ga}_{1-x}\text{As}$, although this has not been examined to our knowledge. The energy band diagrams that may be expected for a Ge- $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs structure are then as shown in Fig. 2. From Fig. 2(c) it is seen that there are objectionable spike barriers to the movement of a photoinduced electron from the Ge through the other layers into vacuum. Also there is some problem that the barrier in the valence band against hole injection from the $p^*\text{GaAs}$ into the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ becomes small under bias conditions. There is need for an examination of this system to ascertain the significance of the conduction band barriers and to determine whether with suitable grading their effects may be minimized. The data referred to above are inferred from abrupt junctions between heavily doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and GaAs and may not be true for the lightly doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ envisioned for this study.

With the Ge/ZnSe/GaAs (Cs) structure proposed it seems reasonable to expect electron emission for

photons down to the Ge absorption edge ~ 0.7 eV. The device therefore should cover the important laser lines at 1.06μ (Nd), 1.15μ (HeNe), and 1.69μ (Ar). It should also operate comfortably in the atmospheric windows up to the $1.4\text{--}1.8\text{-}\mu$ window. In Fig. 1(b) we have envisaged the photons applied to the back side of the Ge substrate (~ 0.015 in. thick); however, the possibility exists that the photons could enter through the Cs face and penetrate the $p^*\text{GaAs}$ and the ZnSe layers before absorption in the Ge. Since the GaAs is heavily doped some losses by free carrier absorption may be anticipated in this layer.

It is desirable that the Ge be p type doped to prevent injection of electrons from the Ge into the ZnSe by the applied bias voltage V_{12} of Fig. 1(b) from obscuring the photoinduced emission. However by making the Ge n type, the structure should become a cold-cathode emitter of electrons, with the emission controlled by the voltage V_{12} .

*Work supported in part by the Army Research Office, Durham.

¹R. L. Bell and W. E. Spicer, Proc. IEEE 58, 1788 (1970).

²Zh. I. Alferov, Akadémiai Kiadó 2, 7(1971).

Proposed Third-Harmonic Generation in Phase-Matched Metal Vapors*

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(Received 30 August 1971)

This letter considers the use of alkali metal vapors, phase matched with inert buffer gases for generation of third-harmonic radiation. For example, calculations show that 1.8 MW will be required for 50% conversion of $1.06\text{-}\mu$ radiation to $0.35\text{-}\mu$ radiation using a 1:412 part mixture of rubidium and xenon. Generation to frequencies above the ionization potential of the metal vapors is considered.

This letter proposes a technique for the efficient production of ultraviolet radiation by third-harmonic generation in phase-matched metal vapors. As a result of their large oscillator strengths and resonant frequencies located in the visible region of the spectrum, we calculate nonlinear susceptibilities about 10^5 times greater than those of the inert gases which have been previously studied.¹ Of key importance, the high localized oscillator strengths of vapors such as Rb, Cs, Na, etc., cause their refractive indices at frequencies below their fundamental resonance lines to be greater than their refractive indices at the third harmonic of these frequencies.² It is then possible to add an inert buffer gas to attain phase matching ($n_1 = n_3$). Calculations show the ratio of the necessary partial pressure of metal vapor to buffer gas to typically be about 1:400. Other potentially

interesting features of the metal-vapor inert-gas system are wide acceptance bandwidth and thus the ability to utilize subpicosecond pulses; and the ability to generate to frequencies above the metal-vapor ionization potential and thus to regions of the uv where most solids or liquids are opaque. The possibility of using anomalous dispersion to achieve phase matching was noted by a number of early workers,³ and has been demonstrated in liquids by Bey *et al.*⁴

The principal results of this letter are summarized in Table I and will be discussed in the paragraphs below. We consider three possible tripling experiments, i.e., $10640 \rightarrow 3547 \text{ \AA}$ in Rb and $6943 \rightarrow 2314 \text{ \AA}$ and $6000 \rightarrow 2000 \text{ \AA}$ in Na. In each case, the number of metal atoms/cc is chosen to yield a maximum transmission loss at the fundamental or third harmonic of

TABLE I. Calculated parameters for third-harmonic generation in metal vapors.

$\lambda_F \rightarrow \lambda_{3rd}$	10 640 \rightarrow 3547 Å	6943 \rightarrow 2314 Å	6000 \rightarrow 2000 Å
Metal vapor	Rb	Na	Na
Buffer Gas	Xe	Xe	Xe
Metal atoms/cc ^a	2.25×10^{17}	7.73×10^{16}	2.12×10^{16}
Partial pressure of metal vapor (mm Hg)	16.0	6.40	1.61
Cell temperature	415 °C	527 °C	461 °C
$\chi_{\text{metal vapor}}$ (esu)	7.42×10^{-32}	5.86×10^{-33}	-6.36×10^{-33}
L_c (cm)	9.62×10^{-2}	2.60×10^{-1}	1.10×10^{-1}
Number atoms buffer gas	$\frac{412}{1}$	$\frac{100}{1}$	$\frac{476}{1}$
Number atoms metal vapor			
P_F/A (50% conversion, $L = 50$ cm) (W/cm ²)	7.27×10^8	1.75×10^{10}	5.07×10^{10}
P_F (50% conversion) (W)	1.93×10^6	3.04×10^7	7.61×10^7
α_F (cm ⁻¹)	4.17×10^{-3}	2.13×10^{-4}	5.74×10^{-3}
α_{3rd} (cm ⁻¹)	5.74×10^{-3}	5.74×10^{-3}	3.73×10^{-4}
P_{sat}/A (W/cm ²)	1.68×10^8	3.24×10^9	3.82×10^7
J_{sat}/A (J/cm ²)	5.04	51.8	0.611
Δt_{min} (sec)	3.80×10^{-13}	1.43×10^{-13}	7.63×10^{-12}

^aNumber of metal-vapor atoms adjusted for maximum loss of 25% for 50 cm at fundamental or third-harmonic wavelengths.

25% in a 50-cm-long cell in the presence of the higher pressure buffer gas which is necessary for phase matching.

Calculations of the third-harmonic nonlinearity were carried out using the formula of Armstrong *et al.*,³ i. e.,

$$\chi(3\omega, \omega, \omega, \omega) = (e^4/\hbar^3) \sum_{ijkl} A_{ijk} Z_{gi} Z_{ij} Z_{jk} Z_{kg} \quad (\text{esu}), \quad (1)$$

where the A_{ijk} are frequency-dependent coefficients with resonant denominators at $(\omega_{gp} - \omega)$, $(\omega_{gp} - 2\omega)$, and $(\omega_{gp} - 3\omega)$, where ω is the fundamental laser frequency and ω_{gp} corresponds to any atomic transition frequency to ground. To evaluate (1) all terms (a total of 128) involving all levels between the 5s and 7d states for Rb and between the 3s and 6d states for Na were retained. Magnitudes of matrix elements were obtained from calculated oscillator strengths,^{5,6} while the signs of matrix elements were determined from the tables of Bates and Damgaard.⁷ The fine splitting of a multiplet was accounted for via degeneracy factors and a weighted average frequency. The calculated magnitudes of $\chi(3\omega, \omega, \omega, \omega)$ are given on line 7 of Table I.

The refractive indices of the metal vapors were calculated from the standard Sellmeier formulas and are in agreement with the early experimental data of Wood.² (It is of interest to note that the refractive index of Na is less than 1 over the wavelength region $\lambda = 5890$ Å to $\lambda = 3320$ Å.) The coherence length ($L_c = \lambda_F/6\Delta n$) for third-harmonic generation for a non-phase-matched metal vapor is given on line 8 of

Table I, and corresponds to the metal-vapor pressure given on line 5.

To obtain phase matching and thus to increase the conversion efficiency by $(L/L_c)^2$ we add a normally dispersive buffer gas at a partial pressure to cause the refractive indices at the fundamental and third-harmonic frequencies to be equal. Refractive indices for Xe were obtained from the formula of Kock.⁸ Line 9 of Table I gives the ratio of the number of atoms of Xe to the number of atoms of metal vapor which is necessary to obtain phase matching.

Assuming no depletion of the fundamental, the ratio of generated third-harmonic power to incident fundamental power is given in mks units by

$$\frac{P_3}{P_1} = \frac{9\pi^2 \eta^4 c^2 L^2 \chi_T^2 (P_1)^2}{4\lambda_1^2 A} \approx \frac{9\pi^2 \eta^4 c^2 \chi_T^2}{\lambda_1^4} P_1^2 \quad (\text{mks}), \quad (2)$$

where $\chi_{\text{mks}} = (10^{-17}) \chi_{\text{esu}}$, $\eta = 377 \Omega$, λ_1 is the wavelength of the fundamental, L is the cell length, and A is the area of all beams. To obtain χ_T in Eq. (2), the per atom χ of line 7 is multiplied by the total number of atoms (all assumed to be in the ground state) and is divided by the total degeneracy of the ground state (two for the alkali metals). To obtain the second equality in Eq. (2) we assume a Gaussian beam with a confocal parameter equal to the cell length L . For such a confocally focused beam the conversion efficiency to the third harmonic is independent of the cell length. Lines 10 and 11 of Table I give the necessary fundamental power density and fundamental power (assuming confocal focusing) which are necessary to obtain 50% conversion effi-

ciency to the third harmonic. These values are based on a cell length of 50 cm and the number of metal-vapor atoms given in line 4.

Absorption loss at both the fundamental and third-harmonic frequencies was computed using the standard formulas for pressure broadened Lorentzian lines, with all transitions to ground which contribute significant loss at either frequency accounted for. Continuum losses were obtained from the experimental data of Ditchburn.⁹ For tripling 1.06 μ in Rb the dominant loss occurred at the third harmonic and was due to the $5s-7d$ transition. For tripling 6943 Å or 6000 Å in Na, the dominant losses are at the third harmonic and fundamental, respectively. It is of particular interest that once past the ionization potential the continuum absorption is very small. For example, at 2000 Å, the absorption cross section for Na is about 1.7×10^{-20} cm². Discrete losses were calculated based on the pressure of xenon necessary to achieve phase matching and make use of the inert gas-alkali pressure broadening data given by Ch'en and Takeo.¹⁰

Lines 13 and 14 of Table I give the saturation power density and saturation energy density for the given operating conditions. If the length of the incident pulse substantially exceeds the decay time of the absorbing level then the saturation power density $P_{\text{sat}}/A = \hbar\omega/2\sigma T_1$ (where σ is the cross section and T_1 is the decay time of the absorbing level) is the power density which will reduce the population difference by 50%. For an incident pulse length less than T_1 , $J_{\text{sat}}/A = (P_{\text{sat}}/A) T_1$ is the energy density for 50% population reduction. Since the inert gases have little quenching effect on the alkali metals,¹¹ T_1 for Rb and Na are about 16 and 30 nsec, respectively. From lines 13 and 10 of Table I we see that saturation power density is of the same order or less than the power density necessary for 50% conversion to the uv. For high conversion efficiencies, it will thus be necessary to work with pulses of length $\ll T_1$. For subnanosecond or picosecond pulses the saturation joule requirement will not pose a problem. Optical breakdown in metal vapors has been studied by Rizzo and Klewe¹² who find a breakdown threshold of 10^9 W/cm² at 10^{17} atoms of Cs for a 65-nsec-long ruby pulse. Wang¹³ has shown that for short pulse lengths breakdown is dependent on energy density (as opposed to power density); thus further suggesting the use of short pulses.

Finally we calculate the minimum allowable width of a picosecond pulse to ensure that the third-harmonic pulse does not separate from the fundamental pulse over the cell length. This minimum width depends on the relative dispersion (group velocity difference) at the fundamental and third harmonic and for 50% walk off of a rectangular pulse is

$$\Delta t_{\text{min}} = \frac{n_1 n_3 L}{c^2} \left(\frac{\partial \omega_2}{\partial k_2} - \frac{\partial \omega_1}{\partial k_1} \right). \quad (3)$$

Dispersions were evaluated numerically, again accounting for all contributing transitions; and for the given operating conditions they are given in line 15 of Table I.

Experiments aimed at demonstrating the ideas of this letter are now being constructed in our laboratory. Other metal-vapor inert-gas systems for generation further into the uv, for example Cd-He for 3547 \rightarrow 1182 Å generation, will also be studied.

The authors gratefully acknowledge helpful discussions with J. F. Young, G. Bjorklund, A. H. Kung, and A. E. Siegman. R. B. Miles gratefully acknowledges the Fannie and John K. Hertz Foundation for its generous support.

*Work sponsored by the Air Force Cambridge Laboratories under Contract No. F19(628)-70-C-0057, and by the U.S. Army Research Office—Durham under Contract No. DAHC04-68-C-0048.

¹J. F. Ward and G. H. C. New, Phys. Rev. 185, 57 (1969).

²R. W. Wood, Phil. Mag. Suppl. 8, 293 (1964).

³J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. 127, 1918 (1962).

⁴Pole P. Bey, John F. Giuliani, and Herbert Rabin, Phys. Rev. Letters 19, 819 (1967).

⁵E. M. Anderson and V. A. Zilitis, Opt. Spectrosc. 16, 211 (1964).

⁶W. L. Wiese, M. W. Smith, and B. M. Miles, Natl. Bur. Std. Report NSRDA-NBS 22, Vol. II, 1969 (unpublished).

⁷D. R. Bates and Agnete Damgaard, Phil. Trans. Roy. Soc. 242, 101 (1949).

⁸John Koch, Kungl. Fysiografiska Sällskapet i Lund Fördhandlingar 19, 173 (1949).

⁹R. W. Ditchburn, P. J. Jutsun, and G. B. Marr, Proc. Roy. Soc. (London) A219, 89 (1953).

¹⁰Shang-Yi Ch'en and Makoto Takeo, Rev. Mod. Phys. 29, 20 (1957).

¹¹E. R. Fisher and G. K. Smith, Appl. Opt. 10, 1803 (1971).

¹²J. E. Rizzo and R. C. Klewe, Brit. J. Appl. Phys. 17, 1137 (1966).

¹³Charles C. Wang and L. I. Davis, Jr., Phys. Rev. Letters 26, 822 (1971).