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134 nm vacuum ultraviolet emission using an Ar/Kr gas mixture excited by a quasi-continuous-wave gas jet discharge

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Abstract. We have developed a vacuum ultraviolet (VUV) lamp at 134 nm with a quasi-point emission geometry using a quasi-continuous-wave (cw) gas jet discharge of an Ar/Kr gas mixture. We have unambiguously identified a new emission continuum centered at 134 nm as a transition of Ar−Kr hetero-nuclear excimers (ArKr*). The VUV emission power of the 134 nm continuum was 10 mW at 21 atm of the total Ar/Kr stagnation gas pressure, at a Kr concentration of 0.1%. Characteristic energy transfer between atoms and dimers plays an important role for the efficient production of ArKr* in such a gas jet discharge.

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Compact vacuum ultraviolet (VUV) light sources of various emission wavelengths with a substantial output power are in high demand in application fields such as advanced materials processing and photochemistry [1–4]. Rare-gas excimers have long been one of the few emission media in the VUV spectral region. Their emission wavelengths in the VUV can be selected by changing relevant rare-gas species. We have developed efficient rare-gas excimer lamps using a rare-gas jet discharge [5–7]. An output power of 300 mW was obtained at 174 nm using a quasi-continuous-wave (cw) Xe gas jet discharge [5]. Its emission geometry was a quasi-point source with a diameter of 3 mm, which would be suitable for short wavelength high-resolution optical lithography. By applying a magnetic field to the Xe plasma, the VUV output power increased to being twice as high as that without the magnetic field, due to the effective contraction of the Xe plasma [6]. We also have experimentally verified that the collisional energy transfer between Xe^* and Xe_2 is a predominant excimer production process in the Xe supersonic gas jet discharge [5, 7].

Selectivity of the emission wavelength is also an important factor for light sources used in practical application fields. We have already observed three different well-known second excimer continua in Ar, Kr and Xe gas jet discharges, which are centered at 126 nm, 147 nm and 174 nm, respectively. Several groups have observed new continua at 135 nm and 154 nm using an electron beam and discharge pumping of mixed rare gases of Ar, Kr and Xe [8–10]. These continua were interpreted as the emissions from ArKr and KrXe, respectively. Neither parametric nor kinetic analysis of these continua, however, has been reported until now. We have also observed a new continuum around 160 nm from a $KrXe^*$ hetero-nuclear excimer in a pulsed silent discharge with a binary mixture of Kr and Xe [11, 12]. The center wavelength of $KrXe^*$, however, has not been identified because of the spectral overlap of other excimer transitions. The use of hetero-nuclear excimers may be an effective method to realize new emission wavelengths in the VUV spectral region. It may be practical that a one-discharge set-up could produce various emission wavelengths by manipulating the gas mixture.

In this paper, we describe a VUV lamp emitting at 134 nm with a quasi-point emission geometry. The lamp was realized using a quasi-cw gas jet discharge of a binary gas mixture of Ar and Kr. The emission spectra in the VUV showed substantial changes by the presence of less than 1% Kr at the Ar stagnation pressure of 21 atm. When the Kr concentration was 0.1%, a new continuum from Ar−Kr hetero-nuclear excimers ($ArKr^*$) centered at 134 nm was unambiguously identified in the relevant VUV spectrum. The spectral bandwidth of the continuum was 8 nm (FWHM), which was narrow enough to minimize the spectral overlap to other excimer continua. The VUV output power of this continuum was 10 mW. This power is comparable to that of an Ar_2 continuum observed in an Ar quasi-cw gas jet discharge with a pulse width of 5 ms (FWHM). We have proposed a kinetic model for the binary gas jet discharge, which includes new dimer excitation processes as well as the conventional three-body collisional process. This model considers collisional processes of dimers with excited atoms and of excimers with atoms to produce homo- and hetero-nuclear excimers. Emission intensities of Ar_2^*, $ArKr^*$ and Kr_2^* were numerically evaluated at Kr gas concentrations between 0 and 10%. The kinetic results tell us

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that the energy transfer between excited atoms and dimers is an efficient and dominant enough process to produce these excimers.

1 Experimental procedure

Figure 1 shows a schematic diagram of the experimental set-up for the quasi-cw gas jet discharge with a binary gas mixture of Ar and Kr. A vacuum chamber was evacuated to less than 10^{-5} Torr by a turbo-molecular pump connected to a rotary pump. A gas injector and a pair of iron electrodes were placed at the center of the chamber. A conical nozzle with a 0.8 mm diameter was attached to the injector head to produce clusters in a supersonic gas jet [5]. Laboratory grade Ar and Kr were mixed in a mixing chamber and injected into the vacuum chamber through the conical nozzle. The Kr concentration was varied between 0 and 1.2%. The stagnation pressure in the injector was 21 atm, which was optimized for the maximum VUV output power in our set-up.

A pair of needle-shaped electrodes were placed 3.5 mm downstream from the nozzle surface. The distance between the electrodes was set at 3.5 mm. A 0.53 μF capacitor was charged with a negative high voltage of 2 kV, which was applied between the electrodes. When the mixed gas was injected with a pulse width of 5 ms (FWHM), the discharge was initiated by the impedance decrease between the electrodes. A glow discharge between the electrodes was stabilized with a 100 kΩ resistor (R_S) inserted in a discharge circuit. The discharge current was monitored with another 300 Ω resistor (R_m). A discharge current of 50 mA was measured, which was insensitive to the Kr concentration. This discharge current stayed almost constant for 5 ms (FWHM), which reflected the gas injection time. The visible emission geometry between the electrodes was spherical with a diameter of 3 mm.

VUV emission from the discharge region was detected by using a visible photomultiplier tube with a sodium salicylate scintillator coupled to a 0.2 m VUV spectrometer. Time-resolved signals of the VUV emission were recorded using a digital oscilloscope. Time-integrated VUV spectral information was acquired by using a box-car integrator connected to an $x-y$ plotter. Absolute VUV emission power with solid angle correction was evaluated by a calibrated VUV photomultiplier tube (Hamamatsu, R927) attached to a calibrated bandpass filter for each wavelength of Ar_2^* and Kr_2^* (Acton Corp., 125, 145-N-1D). Since there are no effective bandpass filters available around 134 nm, estimation of the absolute VUV emission power of ArKr* was based on the above calibrated results. Note that the temporal behaviors of the three excimer emissions (Ar_2^*, ArKr*, and Kr_2^*) had a pulse width of 5 ms (FWHM), which was similar to that of the discharge current.

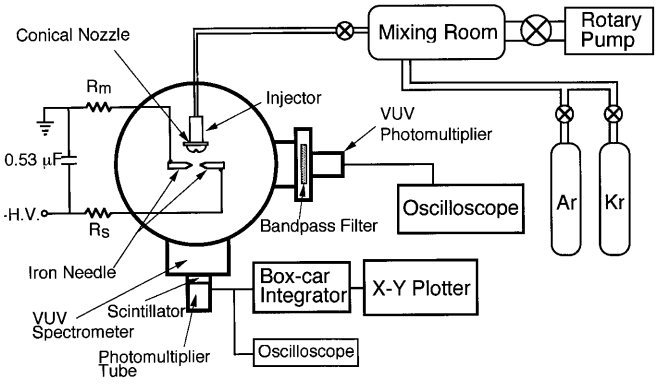

Fig. 1. Schematic diagram of the experimental set-up

2 Ar/Kr mixed gas jet discharge

The time-integrated VUV emission spectral shape was dramatically changed when the Kr concentration was increased, as shown in Fig. 2a–f. This spectrum has not been corrected for the spectral response of the detection system. In Fig. 2a, an Ar_2^* continuum is observed centered at 126 nm, together with resonance atomic lines of Ar* (105 and 107 nm), in the absence of Kr. Note that no ionic lines of rare gases and no emission lines from electrode materials were observed in the spectral region between 100 nm and 250 nm. The output power of this continuum was evaluated to be 16 mW. The electrical input power was 75 W. The power conversion efficiency was thus 0.021%. This high conversion efficiency was mainly attributed to the excimer production process, where Ar* would excite Ar dimers (Ar_2) existing in the supersonic gas jet such as:

$$Ar_2 + Ar^* \rightarrow Ar_2^* + Ar \qquad (1)$$

By increasing Kr concentration to 0.1%, a new continuum attributed to ArKr* was clearly observed at 134 nm (Fig. 2d). A Kr_2^* continuum at 147 nm and the resonance lines of Kr* (116 and 124 nm) and Ar* were observed as well.

Since Ar is approximately three orders of magnitude more abundant than Kr (Fig. 2a–e), the excited argon atoms were the principal excited species in the gas jet plasma regardless

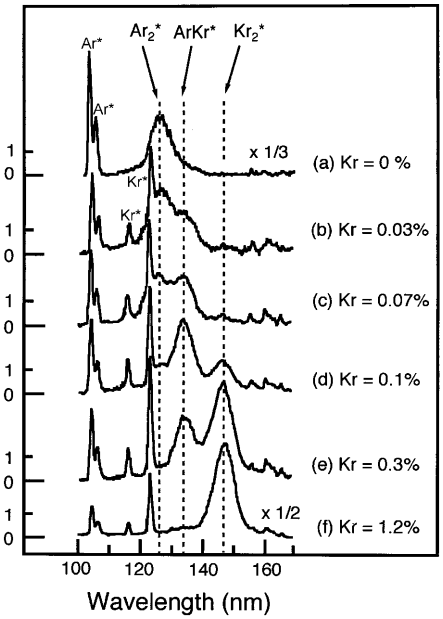

Fig. 2. Emission spectra in the VUV spectral region at different Kr concentrations. The ArKr* has been identified at 134 nm together with well-known Ar_2^* and Kr_2^* excimer emissions

of Kr concentration. The Ar dimer (Ar_2) was also produced almost constantly during the injection of the supersonic gas jet. As long as the excitation process (1) proceeded, the Ar_2^* intensity did not decrease despite the increase in Kr. The fluorescence intensity of Ar_2^*, however, decreased with a slight increase in the Kr concentration. The spectral changes shown in Fig. 2 were caused by fast energy transfer collisions of species existing in a supersonic gas jet of Ar/Kr. The detailed kinetic discussion is given below.

An ArKr* emission power of 10 mW was estimated. This leads to a power conversion efficiency of 0.013%, which is comparable to that of Ar_2^*. The ratio of two different power conversion efficiencies at 0% and 0.1% Kr concentrations (0.01%/0.016%) was 63%, which is comparable to 94% (126 nm/134 nm) of the quantum efficiency of the two continua. The spectral width of 8 nm (FWHM) of the ArKr* continuum was as large as that of Ar_2^* and Kr_2^*, which was narrower than those observed in a silent discharge [12], indicating a lower vibrational temperature [13] than that observed in a silent discharge. Keeping the vibrational temperatures of the excimers low by using the supersonic gas jet was a key to unambiguously identifying a new continuum in the VUV spectral region. Adding Kr up to a concentration of 1.2%, Kr_2^* emission became distinguishable. However, the ArKr* emission disappeared due to the energy transfer process between ArKr* and Kr. (See below.)

3 Kinetic analysis

We have proposed a kinetic model in a binary mixed rare-gas jet discharge to reproduce the experimental results. In a single rare-gas jet discharge, the excitation of dimers by excited rare-gas atoms, which was described in (1), has higher probability than that by the three-body association process such as:

$$Ar^* + 2Ar \rightarrow Ar_2^* + Ar \quad (2)$$

In a binary mixed rare-gas jet discharge, we have included over 30 reaction processes to reproduce the behaviors of ArKr* as well as Ar_2^* and Kr_2^* by preserving the energy conservation law. Figure 3 represents the energy levels and major reactions considered in the kinetic model. Solid lines are of major importance. Six different three-body association processes, other than those represented by (2), and dimer-electron excitation reactions are included in the model, but these are of minor importance and are not shown in Fig. 3. Photoemissions are indicated by wavy arrows. We have justified our kinetic model by comparing the kinetic results with experimental results from single atoms. Rate coefficients for the excitation of dimers were estimated from various collisional energy-transfer processes found in [14] and [15]. The other rate coefficients were taken from [16] and [17]. According to our previous measurement [5], the initial Ar_2 density of $1.9 \times 10^{19}\,cm^{-3}$ was evaluated at the Ar backing pressure of 21 atm. The initial densities of ArKr and Kr_2 were estimated to be $2.8 \times 10^{18}\,cm^{-3}$ and $5.7 \times 10^{17}\,cm^{-3}$, respectively, at the Kr concentration of 1% [18, 19].

The emission intensity of each excimer was calculated using our model. Figure 4 shows the calculated results together with experimental data as a function of the Kr concentration. The calculated intensities of Ar_2^*, ArKr* and Kr_2^* agree well with the experiments. This analysis reveals that the following four energy-transfer processes are especially important for the production and de-excitation of each excimer in the Ar/Kr gas jet plasma.

$$ArKr + Kr^* \rightarrow ArKr^* + Kr \quad (3)$$

$$Ar_2^* + Kr \rightarrow ArKr^* + Ar \quad (4)$$

$$Kr_2 + Kr^* \rightarrow Kr_2^* + Kr \quad (5)$$

$$ArKr^* + Kr \rightarrow Kr_2^* + Ar \quad (6)$$

The Ar_2^* intensity, represented as circles, monotonically decreases as the Kr concentration increases because of the process (4) as well as energy transfer between Ar* and Kr, which are precursors of the relevant excimers. On the other hand, when the Kr concentration increases, the Kr_2^* intensity increases as well, mainly due to processes (5) and (6). The Kr_2^* is the final excited species in our model, and has the lowest internal energy. The ArKr* result shows a peak at a Kr concentration of 0.1%. At a low Kr concentration, Ar_2^* production is predominant although ArKr* is produced even at a Kr concentration of 0.002%. When the Kr concentration becomes high, ArKr* production is overtaken by that of Kr_2^*.

Reaction processes primarily important for producing these excimers are given in Table 1, together with the relevant rate coefficients evaluated using this model. These evaluated rate coefficients are between $10^{-11}\,cm^3s^{-1}$ and $10^{-12}\,cm^3s^{-1}$, which are comparable with those of near-resonant energy-transfer collisional processes between

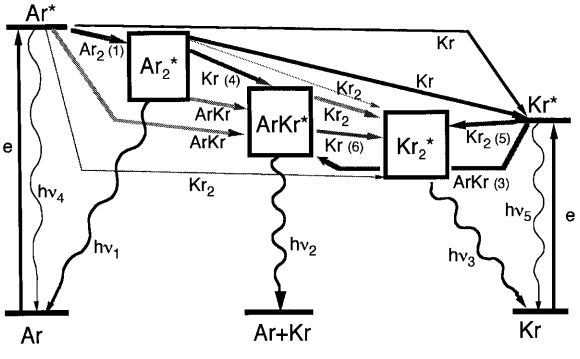

Fig. 3. Energy levels relevant to the excimer production in Ar/Kr gas mixture. Numbers in parenthesis correspond to the reactions in the text

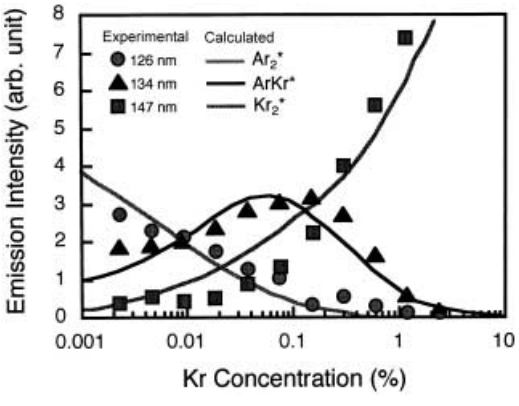

Fig. 4. Comparison between the experimental and kinetic results

Table 1. Major excimer production processes and rate coefficients obtained using the kinetic model

Excimer Species	Production Processes	Rate Coefficients (cm^3s^{-1})
$ArKr^*$	$ArKr + Kr^* \rightarrow ArKr^* + Kr$	3×10^{-11}
	$Ar_2^* + Kr \rightarrow ArKr^* + Ar$	5×10^{-12}
Kr_2^*	$Kr_2 + Kr^* \rightarrow Kr_2^* + Kr$	1×10^{-11}
	$ArKr^* + Kr \rightarrow Kr_2^* + Ar$	6×10^{-12}

atoms [14]. These large rate coefficients lead to the efficient production of $ArKr^*$ and Kr_2^* in the discharge. Despite their low concentration, Krypton atoms play an important role in influencing the excimer production processes.

4 Conclusion

In conclusion, we have developed a new $ArKr^*$ lamp at 134 nm using a quasi-cw gas jet discharge of a binary gas mixture of Ar and Kr. $ArKr^*$ excimer was a predominant VUV emission species at a Kr concentration of 0.1% in Ar. The 134 nm emission power was 10 mW, with a power conversion efficiency of 0.013%. We have proposed a new kinetic model including dimer excitation, which reproduces the experimental results well. Our kinetic analysis reveals that efficient energy transfer collisions occurred with rather high rate coefficients to produce $ArKr^*$. This type of VUV lamp, with various emission wavelengths and with a reasonably high output power would be useful for advanced photon application fields.

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